

# QUANTUM THEORY

## B. AGGREGATES OF PARTICLES

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Edited by

**D. R. DATES**



# **QUANTUM THEORY**

## **A TREATISE IN THREE VOLUMES**

- I.* Elements
- II.* Aggregates of Particles
- III.* Radiation and High Energy Physics



# **QUANTUM THEORY**

## ***II.* Aggregates of Particles**



# QUANTUM THEORY

*Edited by*

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*II.*

*Aggregates of Particles*



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## Preface

*Quantum Theory*, comprising the three volumes, *Elements*, *Aggregates*, and *Radiation and High Energy Physics* is intended as an advanced text and reference on the fundamentals and applications of quantum theory.

It is primarily designed to meet the needs of postgraduate students. The hope is that it will enable them to refresh and deepen their understanding of the elementary parts of the subject, that it will provide them with surveys of the more important areas of interest, and that it will guide them to the main frontiers on which advances are being made. In addition, teachers at universities and institutes of technology may find the compilation, which is unusually wide in scope, useful when preparing lectures.

A knowledge is naturally assumed of classical mechanics, of electromagnetic theory, of atomic physics, and (in Volume III) of the special theory of relativity. Familiarity with the ordinary techniques of mathematical analysis is also assumed. However, the relevant properties of some of the higher transcendental functions are summarized and accounts are given of operator algebra and matrices (Volume I) and of group theory (Volume II).

In Volume I non-relativistic wave mechanics and matrix mechanics are introduced; an extensive survey of the exactly soluble problems of the point and of the continuous spectrum is presented; the approximate methods which are available for treating other stationary and time-dependent problems are then developed in considerable detail; and finally a very lengthy chapter is devoted to scattering theory, the needs of both ionic and nuclear physicists being met. To make this volume useful as a reference the treatment of many of the topics is more comprehensive than is customary; in order that it should nevertheless remain useful as a text the sections containing the essentials are indicated at the beginning of certain of the chapters.

Volume II is concerned with the quantal treatment of systems of particles — complex atoms, molecules, solids, and liquids. A chapter on quantum statistics is included. It is hoped that theoretical chemists, as well as theoretical physicists, will find the volume of value. Like the other volumes, it is effectively complete in itself.

In Volume III the compilation returns to the fundamentals of quantum theory. The relativistic equations describing a single particle in an external field of force are developed; starting with the semiclassical theory a detailed exposition is given of both the noncovariant and the covariant theory of radiation; the theory of the meson field is described; and nuclear structure is then discussed. The volume ends with a chapter on the question of whether there are hidden variables underlying quantum theory. It is recognized that the views expressed in this chapter are not widely accepted; but they are undoubtedly stimulating.

A treatise by a group of authors is likely to have defects which would be avoided in a text by a single author. The Editor believes that a compensatory advantage is gained by having research workers writing on parts of the subject in which they are particularly interested.

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## 1. Introductory Survey

### 1.1 Lines and Levels

The most detailed information concerning the structure of complex atoms is obtained from spectroscopic observations. One may explain a large number of lines in an atomic spectrum by postulating the existence of a smaller number of energy levels. With energies  $E_a$  the line frequencies are given by  $h\nu_{aa'} = |E_a - E_{a'}|$ . An atom with energy  $E_g$ , where  $E_g$  is the smallest of the  $E_a$ , is said to be in the ground state. In many spectra one observes spectral series in which the separation of successive lines decreases uniformly with increasing frequency and tends to zero at a definite spectral limit corresponding to an energy  $E_\infty$ ; beyond this limit a continuous spectrum may be observed.

The reality of energy levels is confirmed by electron impact studies; with electrons of kinetic energy  $\frac{1}{2}mv^2$  incident on ground state atoms a line of frequency  $\nu_{aa'}$  is observed only when  $\frac{1}{2}mv^2$  is at least as great as  $(E_a - E_g)$ . As soon as the kinetic energy exceeds  $(E_\infty - E_g)$  it is found that collisional ionization can occur; the spectral limit  $E_\infty$  therefore corresponds to an ionization limit.

## 1.2 Selection Rules

Once the energy level scheme has been obtained it is found that many transitions between levels are not observed as spectral lines. One may therefore suppose radiative transitions to be governed by certain selection rules. The theory of atomic structure must explain, not only the existence of energy levels, but also the selection rules governing transitions between levels and the great variations of intensity of the observed lines.

## 1.3 The Bohr Theory

From a classical standpoint atomic spectra remained largely inexplicable; many of the problems presented are of an essentially quantum mechanical nature. Bohr, in the first major theoretical advance, postulated that electron angular momentum was quantized according to the rule  $L = n\hbar$  with  $n$  integer. He supposed a hydrogenic atom to be composed of a massive nucleus of charge  $Ze$  and an electron of charge  $-e$ . Assuming the laws of non-relativistic classical mechanics, with electrostatic interactions the only forces between the particles, the energy levels were found to be given by

$$E_n = -\frac{1}{2} \times \frac{Z^2}{n^2} \times \frac{e^2}{a_0} \quad (1)$$

and the radii of circular orbits by

$$r_n = \frac{n^2}{Z} \times a_0 \quad (2)$$

In place of energies it is often convenient to use *term values* defined by

$$T_n = -\frac{E_n}{hc} \quad (3)$$

The  $T_n$  will then be positive numbers and, with  $E_n$  in cgs units,  $T_n$  will be in units of  $\text{cm}^{-1}$ . From (1),

$$T_n = R \frac{Z^2}{n^2} \quad (4)$$

with

$$R = \frac{1}{2} \times \frac{e^2}{a_0} \times \frac{1}{hc} = 109737 \text{ cm}^{-1}. \quad (5)$$

Introducing the fine-structure constant  $\alpha = e^2/c\hbar$  we may put  $R = \alpha/4\pi a_0$ .



For the wave number (reciprocal of the wavelength) of a hydrogen line  $n \rightarrow n'$  we obtain

$$\sigma_{nn'} = RZ^2 \left( \frac{1}{n'^2} - \frac{1}{n^2} \right)$$

The above formulas apply in the limit of an infinitely massive nucleus. With a nucleus of mass  $M$  we must use the reduced mass  $mM/(m + M)$  in place of the electron mass  $m$ . This means that  $R$  must be replaced by

$$R_M = \frac{R}{1 + (m/M)}$$

The Bohr theory, with  $Z = 1$  and  $M$  equal to the proton mass, is then in good agreement with observed hydrogen wave numbers so long as fine structure, observed at very high resolution, is not considered.

#### 1.4 Atomic Units

We define the atomic units of mass, length, and time on putting  $m = e = \hbar = 1$ ; in these units  $E_n = -Z^2/2n^2$  and  $r_n = n^2/Z$ . The atomic length unit is  $a_0 = 0.5292 \times 10^{-8}$  cm and the atomic energy unit is  $e^2/a_0$  which is equal to 27.20 eV or *twice* the ionization energy of the hydrogen ground state. The fine structure constant,  $\alpha = e^2/c\hbar$ , is a dimensionless number approximately equal to  $1/137$ . In atomic units the velocity of light is therefore  $c \simeq 137$ .

#### 1.5 Relativistic Effects

In atomic units the Bohr angular momentum condition for circular orbits is  $L = v_n r_n = n$ . Therefore  $v_n = Z/n$  and  $(v_n/c)^2 \simeq (Z/137n)^2$ . It follows that  $(v_n/c)^2$  will be small for  $Z$  small and, in consequence, a non-relativistic theory should provide a good approximation.

#### 1.6 Magnetic Moments and Spin-Orbit Energy

A circulating current  $i$  produces a magnetic moment  $\mu = iA/c$  where  $A$  is the area of the current circuit described in the usual vector sense (Fig. 1). For an electron of charge  $-e$  circulating with velocity  $v$  in an orbit of radius  $r$  the mean current is  $i = -ev/2\pi r$  and the area is  $A = \pi r^2$ . The magnetic moment is therefore  $\mu = -er \times v/2c$ . Introducing the momentum  $p = mv$  and the angular momentum  $L = r \times p$  we obtain

$$\mu_L = -\frac{e}{2mc} L. \quad (6)$$

This is the magnetic moment associated with an electron orbital angular momentum  $\mathbf{L}$ . An electron also has a spin angular momentum  $\mathbf{S}$  and an associated spin magnetic moment

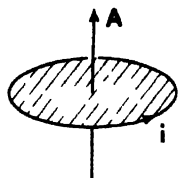


FIG. 1.

$$\mu_s = - \frac{2mc}{2} \mathbf{S}. \quad (7)$$

The spin magnetic moment is said to be *anomalous* because  $(\mu_s/S)$  is *twice*  $(\mu_L/L)$ .

The interaction energy between a magnet of moment  $\boldsymbol{\mu}$  and a magnetic field  $\mathbf{H}$  will be  $-\boldsymbol{\mu} \cdot \mathbf{H}$ . Consider a magnet moving with momentum  $\mathbf{p}$  in an electric field  $\mathbf{E}$ .

In a frame of reference fixed relative to the magnet there will be a magnetic field\*  $\mathbf{H} = (\mathbf{E} \times \mathbf{p})/mc$  and the classical interaction energy will be  $-\boldsymbol{\mu} \cdot \mathbf{H}$ . If the magnetic moment is due to electron spin a relativistic treatment<sup>2</sup> shows that the interaction energy is  $-\frac{1}{2} \boldsymbol{\mu}_s \cdot \mathbf{H}$ . Consider an electron moving in a central field with potential energy  $V(r)$ . The electrostatic potential per unit charge will be  $-V/e$  and the electric field will be  $\mathbf{E} = -\text{grad}(-V/e)$  from which we obtain

$$\mathbf{E} = \frac{1}{er} \frac{\partial V}{\partial r} \mathbf{r}.$$

The magnetic field which interacts with the spin magnetic moment is therefore

$$\mathbf{H} = \frac{1}{mc} \mathbf{E} \times \mathbf{p} = \frac{1}{emc} \frac{1}{r} \frac{\partial V}{\partial r} \mathbf{L},$$

$\mathbf{L}$  being  $\mathbf{r} \times \mathbf{p}$ , and the interaction energy is

$$\Delta E_{\text{sp}} = -\frac{1}{2} \boldsymbol{\mu}_s \cdot \mathbf{H} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{\partial V}{\partial r} \mathbf{S} \cdot \mathbf{L}. \quad (8)$$

This is known as the *spin-orbit interaction*. The expression (8) may be obtained† using Dirac's theory of the electron.

For hydrogenic ions

$$\frac{1}{r} \frac{\partial V}{\partial r} = \frac{Ze^2}{r^3}$$

\* The transformation required to obtain this result is discussed by Heitler.<sup>1</sup>

† See Condon and Shortley,<sup>2</sup> p. 130.

The component of  $\mathbf{S}$  in any given direction may take the values  $\pm \frac{1}{2}\hbar$ . To obtain an order of magnitude estimate\* of  $\Delta E_{\text{sp}}$  we put

$$\mathbf{S} \cdot \mathbf{L} \simeq \frac{1}{2} \hbar L_n = \frac{1}{2} \hbar^2 n.$$

With  $r = r_n = n^2/Z$  we then obtain

$$\Delta E_{\text{sp}} \simeq \frac{Z^4}{4(137)^2 n^5}$$

in atomic units. Since  $(v_n/c)^2 \simeq (Z/137n)^2$  we may expect that, for small  $Z$ , the spin-orbit energy will be of a magnitude comparable with that arising from other magnetic and relativistic effects. For larger values of  $Z$ , however, we may expect the spin-orbit energy to be the most important correction to the nonrelativistic theory in which only electrostatic forces are considered.

For light atoms the spin-orbit energy will be small compared with the electrostatic energy. One may therefore calculate the wave functions for light atoms taking only electrostatic energies into account and then estimate the spin-orbit energy using perturbation methods.

### 1.7 Nuclear Charge

The Bohr theory gives agreement with observed frequencies for the following ions and assigned  $Z$  values:

Ion	H	He <sup>+</sup>	Li <sup>++</sup>	Be <sup>+++</sup>	B <sup>++</sup>
$Z$	1	2	3	4	5

This suggests that the atomic number, as determined by the sequence of elements in the periodic table, is equal to the nuclear charge  $Z$ . Confirmation is provided by other evidence, such as  $\alpha$ -particle scattering and X-ray spectra. The number of electrons will be denoted by  $N$ . For neutral atoms  $N$  will be equal to  $Z$ , for positive ions  $N$  will be less than  $Z$  and for negative ions  $N$  will be greater than  $Z$ .

### 1.8 Schrödinger Equation

For an  $N$ -electron atom with nuclear charge  $Z$  the nonrelativistic Schrödinger equation is

$$\left\{ -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) - E \right\} \psi = 0. \quad (9)$$

\* A more exact treatment will be given in § 3.5.

Considering only electrostatic interactions the potential energy is

$$V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = -Ze^2 \sum_{i=1}^N \frac{1}{r_i} + e^2 \sum'_{i,j=1}^N \frac{1}{r_{ij}} \quad (10)$$

where  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ . A coordinate system is used with the nucleus, assumed to be of infinite mass, at the origin. We use the notation  $\sum'_{i,j}$  to denote a sum over all pairs  $(i, j)$ , each pair being counted once only and  $i = j$  being excluded: one may put

$$\sum'_{i,j=1}^N = \sum_{i=1}^N \sum_{j=1}^{N-1} \quad (11)$$

The wave mechanical theory for hydrogenic ions (Vol. I, Chapter 3, § 5.1.1) is obtained on putting  $N = 1$  and  $V(r) = -Ze^2/r$  in (9). One obtains the expression (1) for the energy levels but  $n$  is no longer interpreted as an angular momentum quantum number.

### 1.9 Procedure and References

Exact solutions of the Schrödinger equation have not been obtained for  $N \geq 2$ . For He and other light systems, however, elaborate variational calculations give energies which, with relativistic and spin corrections, are of an accuracy comparable to that of the best experimental determinations. For heavier systems more drastic approximations are necessary. The approach adopted is often suggested by physical as much as by purely mathematical considerations.

We begin by considering the central field model and the interpretation of alkali spectra. Electron spin variables are introduced at an early stage for the reason that, even although the energy directly associated with electron spin may be small, the spin variables are of fundamental importance in connection with the symmetry properties of atomic wave functions. The Pauli exclusion principle is advanced as a postulate which enables the structure of the periodic table to be understood. It is then shown how the essential content of the exclusion principle may be restated in a more general form.

A clear understanding of the elements of perturbation theory is needed for the study of complex atoms. The theory of angular momentum coupling, discussed in § 7, is also essential. Complex atomic configurations are discussed in § 8 to § 12. The last two sections deal with the calculation of atomic wave functions and with the theory of radiative transition probabilities.

White's "Introduction to Atomic Spectra"<sup>4</sup> and Herzberg's "Atomic Spectra and Atomic Structure"<sup>5</sup> are recommended for accounts of the basic physics and more elementary accounts of the theory. A useful discussion of the foundations of the theory is given by Eyring, Walter, and Kimball.<sup>6</sup> The standard theoretical work is "The Theory of Atomic Spectra" by Condon and Shortley.<sup>3</sup> Since the appearance of this book the most important theoretical advance is the introduction of tensor operator methods by Racah.<sup>7</sup> Valuable accounts of the quantum theory of angular momentum and of tensor operator theory are contained in the recent books by Edmonds<sup>8</sup> by Rose<sup>9</sup> and by Fano and Racah.<sup>22</sup> An excellent account of atomic structure calculations is given in a recent book by Hartree.<sup>10</sup>

## 2. The Central Field Model

### 2.1 The Physical Idea

In order to obtain approximate solutions of the Schrödinger equation (9) the first step is to choose a suitable simplified form for the wave function. The "best" wave function consistent with this form may be determined later using variational methods. In the central field model each electron is considered to move in the field of the nucleus and a mean central field due to the charge clouds of the other electrons. If electron\*  $i$  moves in the field  $v_i(r_i)$  the total potential energy will be

$$V = \sum_{i=1}^N v_i(r_i). \quad (12)$$

On substituting this potential in (9) we obtain an equation in which the variables are separable. A solution will be

$$\psi = \varphi_1(r_1)\varphi_2(r_2) \dots \varphi_N(r_N) \quad (13)$$

where

$$-\frac{\hbar^2}{2m} \nabla_i^2 + v_i(r_i) - E_i \mid \varphi_i(r_i) = 0 \quad (14)$$

and

$$E = \sum E_i. \quad (15)$$

\* For the moment electrons are assumed to be distinguishable particles. Electron  $i$  means the electron with coordinate  $r_i$ .

## 2.2 Self-Consistent Field

Let us suppose that solutions of the Eq. (14) have been obtained and normalized to unity. The charge density due to electron  $i$  will be  $-e|\varphi_i(\mathbf{r}_i)|^2$  and the potential for electron  $j$  will be

$$v_j(r_j) = -\frac{Ze^2}{r_j} + \sum_{i \neq j} e^2 \int |\varphi_i(\mathbf{r}_i)|^2 \frac{1}{r_{ij}} d\tau_i \quad (16)$$

where  $d\tau_i = dx_i dy_i dz_i$ . The requirement that  $v_j$  should be spherically symmetric may be met by neglecting any nonspherically symmetric terms on the right-hand side of (16).

It is seen that, given the potentials  $v_i$ , the wave functions  $\varphi_i$  may be calculated and that, given the wave functions, the potentials may be calculated. By iterative numerical methods self-consistent solutions may be obtained. This is the self-consistent field method of Hartree<sup>10</sup>; it will be discussed further in § 12.

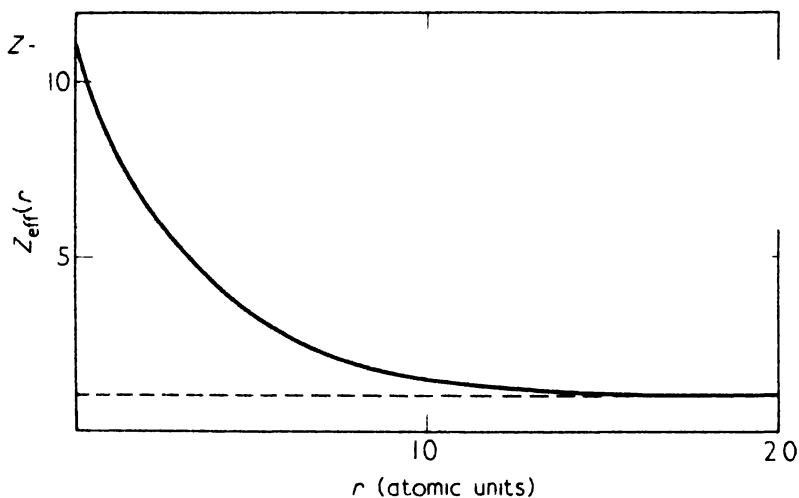


FIG.2. The effective charge  $Z_{\text{eff}}(r)$ . When  $r = 0$ ,  $Z_{\text{eff}}$  is equal to the nuclear charge  $Z$  and when  $r \rightarrow \infty$ ,  $Z_{\text{eff}}$  tends to the residual charge  $z = (Z - N + 1)$  (The curve given is that calculated by the Hartree-Fock method (§ 10.13.5) for the valence-electron potential of Na.)

## 2.3 The Central Field Equation

This equation is

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v(r) - E_n \right\} \varphi(\mathbf{r}) = 0. \quad (17)$$

The potential  $v(r)$  may be written

$$v(r) = - \frac{e^2 Z_{\text{eff}}(r)}{r} \quad (18)$$

The behaviour to be expected for  $Z_{\text{eff}}(r)$ , as deduced from (16), is shown schematically in Fig. 2. For  $r = 0$  we have  $Z_{\text{eff}}(0) = Z$  and for large  $r$  we have  $Z_{\text{eff}} \rightarrow z$  where  $z = (Z - N + 1)$ ;  $z$  will be termed the *residual charge*. For neutral atoms  $z = 1$ .

## 2.4 Spherical Harmonics

Equation (17) permits a further separation of variables on introducing polar coordinates. We put  $\mathbf{r} = (r, \theta, \varphi) = (r, \hat{\mathbf{r}})$  where the unit vector  $\hat{\mathbf{r}} = (\mathbf{r}/r)$  may be used in place of the polar angles  $\theta, \varphi$ . The solutions of (17) may be written

$$\varphi(nl m_l | \mathbf{r}) = Y_{lm_l}(\hat{\mathbf{r}}) \frac{1}{r} P_{nl}(r) \quad (19)$$

where  $Y_{lm_l}(\hat{\mathbf{r}})$  is a normalized spherical harmonic defined by\*

$$\begin{aligned} Y_{l|m_l|}(\hat{\mathbf{r}}) &= (-1)^{|m_l|} \frac{\exp(i|m_l|\varphi)}{(2\pi)^{1/2}} \left[ \frac{(2l+1)(l-|m_l|)!}{2(l+|m_l|)!} \right]^{1/2} P_l^{|m_l|}(\cos \theta) \\ Y_{l-|m_l|}(\hat{\mathbf{r}}) &= + \frac{\exp(-i|m_l|\varphi)}{(2\pi)^{1/2}} \left[ \frac{(2l+1)(l-|m_l|)!}{2(l+|m_l|)!} \right]^{1/2} P_l^{|m_l|}(\cos \theta). \end{aligned} \quad (20)$$

It may be noted that  $Y_{00} = 1/(4\pi)^{1/2}$  and that

$$\begin{aligned} Y_{11} &= - (3/8\pi)^{1/2} e^{i\varphi} \sin \theta, & Y_{10} &= (3/4\pi)^{1/2} \cos \theta, \\ Y_{1-1} &= (3/8\pi)^{1/2} e^{-i\varphi} \sin \theta. \end{aligned} \quad (21)$$

The orthonormality relations for the  $Y_{lm_l}$  may be written

$$\int Y_{l'm_l'}^*(\hat{\mathbf{r}}) Y_{lm_l}(\hat{\mathbf{r}}) d\hat{\mathbf{r}} = \delta_{ll'} \delta_{m_l m_l'} \quad (22)$$

where  $d\hat{\mathbf{r}} = \sin \theta d\theta d\varphi$ . The spherical harmonics form a complete set of functions in the "space" of the angular coordinates  $\hat{\mathbf{r}} = (\theta, \varphi)$ ; hence the angular dependence of any one-electron wave function may always be represented by a linear combination of spherical harmonics. The inter-

\* It should be noted that a definite phase choice is made in the definition of  $Y_{lm_l}$ ; this will be discussed in § 6.2.

pretation of  $l, m_l$  as angular momentum quantum numbers will be discussed further in § 6.

## 2.5 Spin Functions

It is often necessary to include spin variables in the one-electron functions (c.f. Vol I, Chapter 2, § 4.4). We postulate the existence of a spin angular momentum which may have the value in any given direction, conventionally chosen to be the  $Oz$  axis, of  $m_s\hbar$  with  $m_s = \pm \frac{1}{2}$ . We introduce a spin coordinate  $\sigma$  which may be equal to  $\pm \frac{1}{2}$  and the spin functions  $\delta(m_s|\sigma)$ . These are delta functions in the sense that  $\delta(m_s|\sigma)$  is zero for  $m_s \neq \sigma$  and unity for  $m_s = \sigma$ . The orthonormality relation for these functions is

$$\sum_{\sigma = \pm \frac{1}{2}} \delta(m_s|\sigma) \delta(m'_s|\sigma) = \delta_{m_s m'_s}. \quad (23)$$

The functions  $\delta(m_s|\sigma)$  form a complete orthonormal set in the "spin space"  $\sigma$ , any spin state of an electron may be represented in terms of a linear combination of the functions  $\delta(m_s|\sigma)$ .

## 2.6 One-Electron Orbitals

When spin is included the one-electron functions may be written

$$\varphi(nl m_l m_s | \mathbf{x}) = \delta(m_s|\sigma) Y_{lm_l}(\hat{\mathbf{r}}) \frac{1}{r} P_{nl}(r). \quad (24)$$

For the coordinates we use the single symbol  $\mathbf{x} = (\mathbf{r}, \sigma)$ .

More generally we may consider one-electron functions  $\varphi(\alpha|\mathbf{x})$  where  $\alpha$  might stand for the set of quantum numbers  $(nl m_l m_s)$  or might stand for some other convenient set of quantum numbers. The  $\varphi(\alpha|\mathbf{x})$  are termed *one-electron orbitals*. Any function  $\varphi(\alpha|\mathbf{x})$  may be expressed as a linear combination of functions of type (24).

For any operator  $P$ , one electron matrix elements may be written

$$(\alpha|P|\alpha') = \int \varphi^*(\alpha|\mathbf{x}) P \varphi(\alpha'|\mathbf{x}) d\mathbf{x} \quad (25)$$

where  $\int \dots d\mathbf{x}$  means an integration over the spatial coordinates  $\mathbf{r}$  and a sum over the spin coordinates  $\sigma$ . In particular

$$(\alpha|\alpha') = \int \varphi^*(\alpha|\mathbf{x}) \varphi(\alpha'|\mathbf{x}) d\mathbf{x}.$$

An orbital will be normalized if  $(\alpha|\alpha) = 1$ .



## 2.7 Radial Functions

The radial functions  $P_{nl}(r)$  in (24) will be solutions of

$$\frac{d^2}{dr^2} \quad l(l+1) \quad u(r) - \epsilon_{nl} \mid P_{nl}(r) = 0 \quad (26)$$

where

$$u(r) = \frac{2m}{\hbar^2} v(r) \quad \text{and} \quad \epsilon_{nl} = - \frac{2m}{\hbar^2} E_{nl} \quad (27)$$

Since  $E_{nl}$  is negative for bound states,  $\epsilon_{nl}$  will be positive. Numerical methods must be used to obtain solutions of (26) which are everywhere bounded and continuous. Such solutions will exist only for certain discrete eigenvalues of  $\epsilon_{nl}$ ; these must be found by trial and error (practical procedures are discussed by Hartree<sup>10</sup>). The quantum number  $n$  is defined to be such that the number of nodes in the radial function, excluding the origin and infinity, is equal to  $(n - l - 1)$ . This is consistent with the usage of  $n$  for hydrogen. For given  $l$  the function with no nodes has  $n = (l + 1)$ , this is the smallest  $n$  and corresponds to the largest  $\epsilon_{nl}$ .

## 2.8 One-Electron Energies

Having calculated  $E_{nl}$  we define  $Z_{nl}$  by

$$E_{nl} = - \frac{1}{2} \times \frac{Z_{nl}^2}{n^2} \times \frac{e^2}{a_0} \quad (28)$$

Comparison with the hydrogenic formula (1) and with the form of  $Z_{\text{eff}}(r)$  shown in Fig. 2 leads us to expect that  $Z_{nl}$  will be smaller than  $Z$  but greater than the residual charge  $z = (Z - N + 1)$ .

It is important to consider the dependence of  $Z_{nl}$  on  $l$  and on  $n$ . Considering the  $l$ -dependence first, we may expect that  $Z_{nl}$  will be smaller than  $Z_{n'l'}$  if  $l$  is greater than  $l'$ . The physical reason is that an electron with large angular momentum is usually found at large radial distances where  $Z_{\text{eff}}(r)$  is small, whereas an electron with small angular momentum will be more likely to penetrate into the region of large  $Z_{\text{eff}}$ . The mathematical reason is obtained on considering (26) for  $l$  large. The equation will be dominated by the term  $-l(l+1)/r^2$  for  $r$  small and will be sensitive to  $u(r)$  only for large values of  $r$  where  $Z_{\text{eff}}$  is small.

The dependence of  $Z_{nl}$  on  $n$  may be obtained in a similar way. For large  $n$  the electron is most likely to be at large radial distances and therefore  $Z_{nl}$  will be small. Hence  $Z_{nl}$  will decrease with increasing  $n$ .

A formula in many ways more useful than (28) is the Ritz formula

$$E_{nl} = -\frac{1}{2} \cdot \frac{z^2}{(n - \mu_{nl})^2} \cdot \frac{e^2}{a_0^2} \quad (29)$$

which defines the *quantum defect*  $\mu_{nl}$ . The *effective quantum number* is  $n_{nl}^* = n - \mu_{nl}$ . It may be shown<sup>10</sup> that the quantum defect tends to a finite limit as  $n \rightarrow \infty$  and it is usually found that  $\mu_{nl}$  varies slowly with  $n$ . Comparing (28) with (29) and recalling that  $Z_{nl}$  decreases with increasing  $l$ , we may expect  $\mu_{nl}$  to decrease with increasing  $l$ .

## 2.9 Central Field Quantum Numbers

The one-electron central field functions are specified by the quantum numbers  $n, l, m_l, m_s$ , the energy depending only on  $n, l$  and  $l$ . For  $N$  electrons the total energy is

$$E = \sum_i E_{n_i, l_i}$$

The quantum numbers

$$n_1 l_1, n_2 l_2, \dots, n_N l_N$$

are referred to as the *configuration*. Two or more electrons which have the same quantum numbers  $n, l$  are said to be *equivalent*. A configuration of  $q$  equivalent  $nl$  electrons is denoted by  $nl^q$ .

## 3. Spectra of Alkali Atoms

A characteristic of the alkali atoms Li, Na, K, Rb, and Cs is that a single outer electron is readily detached. This is termed the *valence electron*. The evidence for this, other than spectroscopic, includes the low ionization potentials\* (5.39 eV for Li compared with 24.58 eV for He, and 5.14 eV for Na compared with 21.56 eV for Ne), the fact that in the solid state the alkalis are metals (the outer electron explaining the high electrical conductivity), and the tendency of the alkalis to form ionic compounds. We seek to explain the general features of alkali spectra by assuming the model of a single electron moving in a central field. We begin by considering the identification of observed energy levels† in Li.

\* Numerical values for atomic energies are quoted from the tables of Charlotte Moore.<sup>12</sup>

† Our treatment is similar to that given by Herzberg.<sup>5</sup>

### 3.1 The Li Absorption Spectrum

This is obtained on passing light through atomic lithium vapour. With moderate resolution we observe a series of dark absorption lines converging to a spectral limit. This is the *principal series*. The wave numbers will be denoted by  $\sigma_{np}$ , and the wave number of the limit by  $T_{(p)}$ . One obtains  $T_{(p)} = 43487 \text{ cm}^{-1}$ . Assuming the ground state to be the initial state for the absorption process the energy levels required to obtain the principal series are shown in Fig. 3. This assumption requires that  $T_{(p)} = 43487 \text{ cm}^{-1}$  be the term value of the ground state. This agrees with the ionization limit as determined from electron impact studies.

Putting  $\sigma_{np} = T_{(p)} - T_{np}$  it is found that a fair approximation is obtained using the simple hydrogenic formula

$$T_{np} = \frac{R}{n^2} \quad (n \geq 2).$$

A better approximation is

$$T_{np} = \frac{R}{(n - \mu_{np})^2}$$

with  $\mu_{np} = 0.0471$  and almost perfect agreement is obtained with  $\mu_{np} = 0.0471 - 0.0241/n^2$ .

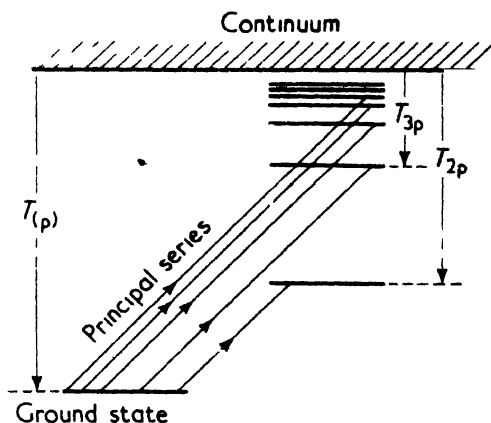


FIG. 3. Energy level diagram for the Li absorption spectrum.

### 3.2 The Li Emission Spectrum

In addition to the principal series at least three other series may be observed in emission; the *sharp* and the *diffuse* series (recognized by the appearance of the lines) and the *fundamental* series with wave numbers close to those of the hydrogen Paschen series ( $n' \rightarrow n = 3$ ). The wave numbers may be represented by the following approximate formulas:

*Sharp series*

$$\sigma_{ns} = T_{(s)} - \frac{R}{(n - \mu_{ns})^2}, \quad T_{(s)} = 28583 \text{ cm}^{-1}, \quad \mu_{ns} \approx 0.40,$$

$$n = 2, 3, 4, \dots$$

*Principal series*

$$\sigma_{np} = T_{(p)} - \frac{R}{(n - \mu_{np})^2}, \quad T_{(p)} = 43487 \text{ cm}^{-1}, \quad \mu_{np} \approx 0.047, \\ n = 2, 3, 4, \dots$$

*Diffuse series*

$$\sigma_{nd} = T_{(d)} - \frac{R}{(n - \mu_{nd})^2}, \quad T_{(d)} = 28583 \text{ cm}^{-1}, \quad \mu_{nd} \approx 0.001, \\ n = 3, 4, 5, \dots$$

*Fundamental series*

$$\sigma_{nf} = T_{(f)} - \frac{R}{(n - \mu_{nf})^2}, \quad T_{(f)} = 12204 \text{ cm}^{-1}, \quad \mu_{nf} = 0.000, \\ n = 4, 5, 6, \dots$$

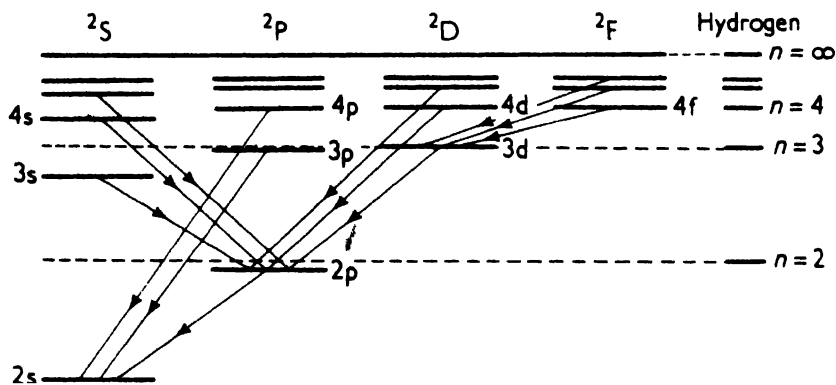


FIG. 4 The Li energy level diagram. The energy levels of H are shown on the right. The diagram shows the first three transitions of the principle series ( $np \rightarrow 2s$ ), the sharp series ( $ns \rightarrow 2p$ ), the diffuse series ( $nd \rightarrow 2p$ ) and the fundamental series ( $nf \rightarrow 3d$ ).

The corresponding energy level diagram is shown in Fig. 4. The diagram and the observed wave numbers are consistent with the relations

$$T_{(p)} = T_{2s}, \quad T_{(s)} = T_{(d)} = T_{2p}, \quad T_{(f)} = T_{3d}.$$

In Fig. 4 we have four series of levels with spectroscopic labels  $s$ ,  $p$ ,  $d$ , and  $f$ . This classification of the observed levels might be expected to be a classification in terms of the quantum numbers  $l$ . Using the fact that the quantum defect  $\mu_{nl}$  decreases with increasing  $l$ , we obtain the following relation between spectroscopic labels and  $l$ -quantum numbers:

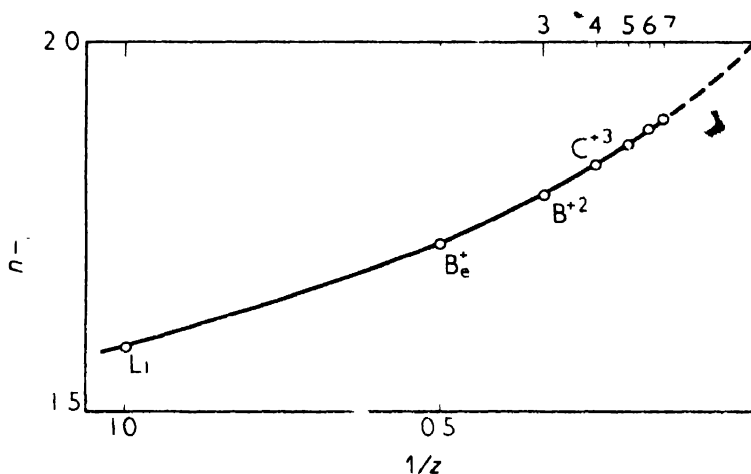
$$l = 0 \quad 1 \quad 2 \quad 3 \\ s \quad p \quad d \quad f.$$

the notation is continued with

$$\begin{array}{cccc} l = & 4 & 5 & 6 & 7 \\ & g & h & i & k. \end{array}$$

The quantum numbers  $nl$  are usually written  $ns, np, nd, \dots$  for  $l = 0, 1, 2, \dots$ . From the diagram (Fig. 4) we obtain the selection rule that all observed lines correspond to a change of  $\pm 1$  in  $l$ .

Our assignment of principal quantum numbers  $n$  agrees with theoretical expectation for  $l = 1, 2, 3$  the lowest  $p$  state being  $2p$ , the lowest  $d$  state  $3d$  and the lowest  $f$  state  $4f$ . There is, however, an apparent anomaly in that the lowest  $s$  state is  $2s$  and not  $1s$ . We say that  $1s$  is an excluded state for valence electron.



5. The effective quantum number ( $n - \mu$ ) for the ground states of the Li iso-electronic sequence. The residual charge  $z$  is 1 for Li, 2 for  $\text{Be}^+$ , 3 for  $\text{B}^{+2}$ ,  $\dots$ . The quantum defects are plotted on a linear scale of  $1/z$ . It is seen that  $(n - \mu)$  tends to 2 as  $z$  tends to infinity.

### 3.3 Ground State Quantum Numbers in the Li Iso-Electronic Sequence

The assignment of principal quantum number 2 for the lowest  $s$  state Li is confirmed by considering the *iso-electronic sequence* Li,  $\text{Be}^+$ ,  $\text{B}^{+2}$ ,  $\text{C}^{+3}$ ,  $\dots$  ions with the same number of electrons but increasing nuclear charge. The corresponding spectra are denoted by Li I, Be II, B III, C IV,  $\dots$ , the Roman numeral being equal to the residual charge  $z$ . For the ground state we put

$$T = \frac{z^2 R}{(n - \mu)^2}$$

and plot the effective quantum number ( $n - \mu$ ) as a function of  $1/z$  (Fig. 5). As the nuclear charge increases the field approximates more closely to the Coulomb form and the quantum defect decreases. It is seen that the effective quantum number tends to 2 as  $z$  goes to infinity.

### 3.4 Other Alkali Atoms

Similar analyses may be made for the other alkalis.\* The selection rules  $\Delta l = \pm 1$  is found to hold but very weak lines are occasionally observed which violate the rule. Table I gives approximate quantum defects  $\mu_{nl}$

TABLE I  
QUANTUM DEFECTS  $\mu_{nl}$  FOR THE ALKALIS

Atom	Series				
	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>
Li	0.40 (2)	0.04 (2)	0.00 (3)	0.00 (4)	—
Na	1.35 (3)	0.85 (3)	0.01 (3)	0.00 (4)	0.00 (5)
K	2.19 (4)	1.71 (4)	0.25 (3)	0.00 (4)	0.00 (5)
Rb	3.13 (5)	2.66 (5)	1.34 (4)	0.01 (4)	0.00 (5)
Cs	4.06 (6)	3.59 (6)	2.46 (5)	0.02 (4)	0.00 (5)

(assumed constant in each  $nl$  series) for the alkali atoms. It is seen that  $\mu_{nl}$  increases with  $Z$  and decreases with  $l$ . Following each quantum defect we give in brackets the value of  $n$  for the lowest level in each series.

### 3.5 Alkali Fine Structure

All alkali levels except  $s$  levels are found to be split into two components, the splitting increasing rapidly with  $Z$ . We seek to explain this in terms of spin-orbit interaction. From (8) we have

$$H_{\text{sp}} = \xi(r) \mathbf{S} \cdot \mathbf{L} \quad (30)$$

for the spin-orbit Hamiltonian,  $\xi(r)$  being

$$\xi(r) = \frac{1}{2m^2c^2} \frac{1}{r} \frac{\partial v}{\partial r} \quad (31)$$

\* Unambiguous identification of the various series depends on consideration of fine structure and of the Zeeman effect. For the assignment of principal quantum numbers of the heavier alkalis more reliance must be placed on theory.

The first step in the calculation of the spin-orbit energy is to introduce the total angular momentum

$$\mathbf{J} = \mathbf{S} + \mathbf{L}.$$

From  $\mathbf{J}^2 = (\mathbf{S} + \mathbf{L})^2$  we obtain

$$\mathbf{S} \cdot \mathbf{L} = \frac{1}{2}(\mathbf{J}^2 - \mathbf{S}^2 - \mathbf{L}^2).$$

Anticipating results to be obtained in § 7 we take the allowed values of  $\mathbf{S} \cdot \mathbf{L}$  to be

$$\hbar^2 [j(j+1) - s(s+1) - l(l+1)]$$

with  $s = \frac{1}{2}$  and  $j = l \pm \frac{1}{2}$ . The second step in the calculation of the spin-orbit energy is to replace  $\xi(r)$  by the mean value  $\int \tilde{P}_{nl}^2 \xi(r) dr$ . Combining these results the expression for the spin-orbit energy is

$$\Delta E(nlj) = \frac{1}{2}[j(j+1) - \frac{3}{4} - l(l+1)]\zeta(nl) \quad (32)$$

with

$$\zeta(nl) = \hbar^2 \int_0^\infty P_{nl}^2(r) \xi(r) dr. \quad (33)$$

The theory therefore predicts a doublet fine structure with separation

$$\delta E(nl) = \Delta E(nlj = l + \frac{1}{2}) - \Delta E(nlj = l - \frac{1}{2}) = \frac{1}{2}(2l+1)\zeta(nl). \quad (34)$$

A difficulty arises in the case of  $s$  states. With  $l = 0$ , the only allowed value of  $j$  is  $+\frac{1}{2}$ . The expression for  $\mathbf{S} \cdot \mathbf{L}$  is zero but the integral (33) is divergent.\* A more exact treatment, using the Dirac relativistic theory (Condon and Shortley,<sup>3</sup> p. 130) shows that the definition (31) of  $\xi(r)$  should be modified for small  $r$  and that the integral for  $\zeta(ns)$  then converges. There is therefore no splitting of  $s$  states but, according to the relativistic theory, there is a shift of  $s$  state energy levels.

The predictions of theory are in agreement with observations. Observed radiative transitions between fine structure levels are found to satisfy the selection rules

$$\Delta j = 0, \pm 1 \quad \text{but not} \quad (j = 0) \rightarrow (j = 0).$$

---

\* It may be recalled that  $P_{nl}(r)$  behaves as  $r^{l+1}$  for small  $r$  and that  $\xi(r)$ , defined by (31), behaves as  $r^{-2}$ ; for  $l = 0$  the integrand of (33) therefore behaves as  $r^{-1}$ .

Taking  $P_{nl}$  to be a hydrogenic function for nuclear charge  $z$  and  $v = -ze^2/r$  one obtains (Condon and Shortley,<sup>3</sup> p. 117)

$$\zeta(nl) = \frac{\hbar^2}{m^2 c^2 a_0^3} n^3 l(2l+1)(l+1)$$

This gives for the term-value difference

$$\delta T_{nl} = -\frac{\delta E(nl)}{\hbar c} = \frac{R\alpha^2 z^4}{n^3 l(l+1)} \quad (35)$$

This agrees with experiment in that it predicts that  $\delta T_{nl}$  should decrease with  $n$  and with  $l$  and should increase with increasing  $z$ .

A quantitative check on the theory may be made<sup>5</sup> for the  $2p$  splitting in the Li isoelectronic sequence. We replace  $z$  in (35) by  $Z_{2p}$  defined by  $T_{2p} = RZ_{2p}^2/4$ . This gives calculated values of  $\delta T_{2p}$  which are compared with observed values in Table II.

TABLE II  
FINE STRUCTURE OF  $2p$  STATES IN THE LI ISOELECTRONIC SEQUENCE

	$\delta T_{2p}(\text{cm}^{-1})$	
	Observed	Calculated
Li	0.338	0.395
Be <sup>+</sup>	6.61	6.39
B <sup>2+</sup>	34.4	32.1
C <sup>3+</sup>	107.4	100.4
N <sup>4+</sup>	259.1	243.1
O <sup>5+</sup>	533.8	500.8

It should be noted that (35) does not give agreement with observed fine structure in hydrogen. This is because other magnetic and relativistic corrections are of the same order as the spin-orbit energy.

### 3.6 The Zeeman Effect

For an alkali atom we continue to consider the model of a single electron moving in a central field. By (6) and (7) the magnetic moment of the atom will be

$$\mu = \frac{e\hbar}{2mc} (L + 2S) = -\frac{e\hbar}{2mc} (J + S)$$





since  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ . If placed in a uniform magnetic field the atom will have an additional energy,

$$\Delta E(\text{mag}) = -\boldsymbol{\mu} \cdot \mathbf{H} = + \frac{e\hbar}{2mc} \cdot (\mathbf{J} + \mathbf{S}) \quad (37)$$

Choosing a coordinate system such that  $\mathbf{H}$  is in the  $Oz$  direction,

$$\Delta E(\text{mag}) = + \frac{e\hbar}{2mc} (J_z + S_z)$$

where  $|\mathbf{H}| = \mathcal{H}$ . From a strict quantum mechanical standpoint we should regard (37) as an additional operator to be included in the Hamiltonian. A perturbation theory treatment of the contribution will be discussed in § 9.1. For the present we consider a more physical approach

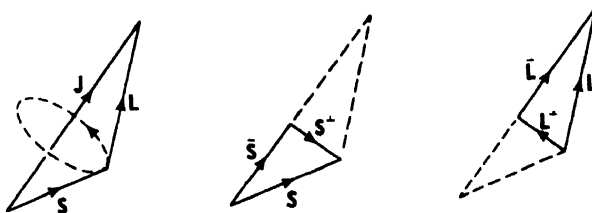


FIG. 6 Coupling of  $\mathbf{S}$  and  $\mathbf{L}$  to give a resultant  $\mathbf{J}$ . In the absence of an external magnetic field  $\mathbf{J}$  is a constant vector and  $\mathbf{S}$  and  $\mathbf{L}$  precess around  $\mathbf{J}$  due to spin-orbit coupling. For the Zeeman effect (weak magnetic field) one considers only the components  $\bar{\mathbf{S}}$  and  $\bar{\mathbf{L}}$  of  $\mathbf{S}$  and  $\mathbf{L}$  which are parallel to  $\mathbf{J}$ .

$\mathbf{J}$  will be a constant vector in the absence of an external field and may still be treated as a constant vector in the limit of a weak field. If the spin magnetic moment were not anomalous (§ 1.6.) the calculation would be very simple. We would have  $\Delta E = (e\hbar/2mc)J_z = (e\hbar/2mc)\hbar m_j$ , assuming the allowed values of  $J_z$  to be  $\hbar m_j$  with  $m_j = j, (j-1), \dots, (-j)$ . This result is not in agreement with experiment, the anomalous magnetic moment must be taken into account. We consider that  $\mathbf{J} = \mathbf{S} + \mathbf{L}$  is a constant vector, that  $\mathbf{S}$  and  $\mathbf{L}$  are constant in magnitude but that, due to spin-orbit coupling,  $\mathbf{S}$  and  $\mathbf{L}$  rotate around  $\mathbf{J}$  (see Fig. 6a). We consider  $\mathbf{S}$  to be the sum of two components, a component  $\bar{\mathbf{S}}$  parallel to  $\mathbf{J}$  and a component  $\mathbf{S}^\perp$  perpendicular to  $\mathbf{J}$  (Fig. 6b). The interaction between  $\mathbf{S}^\perp$  and  $\mathbf{H}$  gives a rapidly fluctuating contribution to the energy which is neglected (it being

assumed that  $S^\perp$  rotates many times around  $J$  during the course of an observation to determine the energy). The parallel component of  $\mathbf{S}$  is

$$\bar{\mathbf{S}} = \frac{(\mathbf{S} \cdot \mathbf{J})\mathbf{J}}{J^2}$$

Considering only this component (37) gives

$$\Delta E = \frac{e\mathcal{H}}{2mc} \left[ 1 + \frac{\mathbf{S} \cdot \mathbf{J}}{J^2} \right] J_z.$$

Since  $L^2 = (\mathbf{S} - \mathbf{J})^2 = S^2 + J^2 - 2\mathbf{S} \cdot \mathbf{J}$  we have

$$\Delta E(\text{mag.}) = \frac{e\mathcal{H}}{2mc} \left[ 1 + \frac{(S^2 + J^2 - L^2)}{2J^2} \right] J_z,$$

and replacing  $S^2, J^2, L^2$  by  $\hbar^2 \frac{1}{2}(\frac{1}{2} + 1), \hbar^2 j(j + 1), \hbar^2 l(l + 1)$  and  $J_z$  by  $\hbar m_j$ ,

$$\Delta E(\text{mag.}) = \frac{e\mathcal{H}}{2mc} g(l) \hbar m_j, \quad (38)$$

where

$$g(l) = 1 + \frac{[\frac{1}{2}(\frac{1}{2} + 1) + j(j + 1) - l(l + 1)]}{2j(j + 1)} \quad (39)$$

is the *Landé g-factor*. These results agree with experiment for fields so weak that  $\Delta E$  (mag.) is small compared with the spin-orbit energy  $\Delta E(nl)$ .

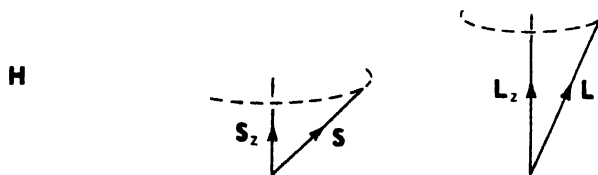


FIG. 7. In the Paschen-Back effect it is assumed that the spin-orbit coupling between  $\mathbf{S}$  and  $\mathbf{L}$  has been broken down by a very large magnetic field. The vectors  $\mathbf{S}$  and  $\mathbf{L}$  precess independently about the direction  $Oz$  of the applied field. Only the components  $S_z$  and  $L_z$  are taken into account when calculating spin-orbit interactions.

### 3.7 The Paschen-Back Effect

We consider an external magnetic field so large that  $\Delta E$  (mag.) is much greater than the spin-orbit energy. The coupling of  $\mathbf{S}$  and  $\mathbf{L}$  to give  $\mathbf{J}$  is then completely broken down and  $J$  does not enter into the theory. Only

the components  $S_z$  and  $L_z$  of  $\mathbf{S}$  and  $\mathbf{L}$  will be constant, since the vectors  $\mathbf{S}$  and  $\mathbf{L}$  rotate around the magnetic field direction (Fig. 7). Replacing  $S_z$  and  $L_z$  by  $\hbar m_s$  and  $\hbar m_l$ , one obtains

$$\Delta E(\text{mag.}) = \frac{e\mathcal{H}}{2mc} (m_l + 2m_s)\hbar.$$

For the spin-orbit energy we consider the operator  $\xi(r)\mathbf{S} \cdot \mathbf{L}$  (§ 3.5.). With the rotating vectors of Fig. 7 only  $S_z L_z$  need be considered, the mean values of  $S_x L_x$  and  $S_y L_y$  being zero. In the Paschen-Back limit the spin-orbit energy is therefore  $\zeta(nl)m_l m_s$ .

#### 4. The Exclusion Principle and the Periodic Table

It has been seen that many properties of the alkali atoms may be understood in terms of a model of a single electron moving in a central field. We may now ask, why is it that the model proves so satisfactory for these particular elements? We consider more generally how the entire structure of the periodic table may be understood. In addition to the idea of the central field model we require the postulate of the Pauli principle.

##### 4.1 The Pauli Exclusion Principle

This states that *no two electrons can be in the same quantum state*. We shall usually consider the quantum states

$$\varphi(nlm_l m_s | \mathbf{x}) = \delta(m_s | \sigma) Y_{lm_l}(\hat{\mathbf{r}}) (1/r) P_{nl}(r).$$

For a given  $nl$  there are  $2(2l+1)$  such states, corresponding to  $m_l = l, (l-1) \dots (-l)$  and  $m_s = \pm \frac{1}{2}$ . It should be emphasized that, so far as the exclusion principle is concerned, there is no necessity to choose the particular set of states\*  $\varphi(nlm_l m_s)$ . The important point is that the functions  $\varphi(nlm_l m_s)$  form a complete set in the sense that any other set of functions for the central field energy level  $nl$  could be expressed as a linear combination of the functions  $\varphi(nlm_l m_s)$  and that the number of linearly independent functions would always be  $2(2l+1)$ .

A *closed shell* is said to exist when  $2(2l+1)$  equivalent electrons occupy all the quantum states of a level  $nl$ .

\* We could, for example, choose functions with angular momenta quantized in the  $Ox$  direction instead of in the  $Oz$  direction.

## 4.2 The Periodic Table

We require the ideas on binding order developed in § 2.8: that, for example, an atomic  $1s$  electron will be the most tightly bound and that a  $2s$  electron will be more tightly bound than a  $2p$  electron.

For the first 36 elements of the periodic table we are led to the assignment of ground configurations shown in Table III. We start with the H  $1s$  ground

TABLE III  
THE PERIODIC TABLE

H	$1s$	Al	$-3s^23p$	Mn	$-3d^54s^2$
He	$1s^2$	Si	$---3p^2$	Fe	$-3d^64s^2$
Li	$1s^22s$	P	$---3p^3$	Co	$-3d^74s^2$
Be	$-2s^2$	S	$---3p^4$	Ni	$-3d^84s^2$
B	$-2s^22p$	Cl	$---3p^5$	Cu	$-3d^{10}4s$
C	$---2p^2$	A	$---3p^6$	Zn	$-3d^{10}4s^2$
N	$---2p^3$	K	$---3p^64s$	Ga	$---4s^24p$
O	$---2p^4$	Ca	$---4s^2$	Ge	$---4p^2$
F	$---2p^5$	Sc	$-3d\ 4s^2$	As	$---4p^3$
Ne	$---2p^6$	Ti	$-3d^24s^2$	Se	$-4p^4$
Na	$---2p^63s$	V	$-3d^34s^2$	Br	$-4p^5$
Mg	$---3s^2$	Cr	$-3d^54s$	Kr	$---4p^6$

state. In He we add a second  $1s$  electron and complete the  $1s^2$  closed shell. The added electron in Li is then  $2s$ . This explains immediately why the  $1s$  state is excluded for the Li valence electron. With Be we complete the  $2s^2$  shell and start adding  $2p$  electrons from B to Ne, the closed  $2p^6$  shell being reached at Ne. With Na we have again an alkali atom, with a  $3s$  electron outside of closed shells. We continue in the same way building up to argon with configuration  $1s^22s^22p^63s^23p^6$ . Many of the regularities of the periodic table, originally deduced from chemical properties of the elements, are immediately apparent. Thus the rare gases He, Ne and Ar have all their electrons in closed shells, and the halogens F and Cl have outer  $np^5$  configurations.

To proceed with the periodic table beyond argon more appeal to experimental evidence is necessary. Thus one might wonder whether a  $4s$  or a  $3d$  electron would be most tightly bound in K. Experiment shows that in fact it is  $4s$ . Further complications arise in the building up of the  $3d$  shell. Thus vanadium, with outer configuration  $3d^34s^2$ , is followed by chromium which has configuration  $3d^54s$  and not  $3d^44s^2$ .

## 5. Symmetry Properties of Atomic Wave Functions

### 5.1 Exchange Symmetry

The Pauli principle was stated in terms of the approximation, based on the central field model, of assigning quantum numbers to each individual electron. We now show that the essential content of the exclusion principle may be restated in a different form which does not depend on the use of approximate models. This form concerns the symmetry of the wave functions for interchange of electron coordinates.

Any function  $f(\mathbf{x}_1, \mathbf{x}_2)$  is said to be symmetric if  $f(\mathbf{x}_1, \mathbf{x}_2) = +f(\mathbf{x}_2, \mathbf{x}_1)$  and to be antisymmetric if  $f(\mathbf{x}_1, \mathbf{x}_2) = -f(\mathbf{x}_2, \mathbf{x}_1)$ . Let  $\psi(\mathbf{x}_1, \mathbf{x}_2)$  be a solution of the Schrödinger equation

$$(H - E)\psi(\mathbf{x}_1, \mathbf{x}_2) = 0 \quad (40)$$

for a two-electron atom. We shall show that  $\psi(\mathbf{x}_1, \mathbf{x}_2)$  must be either symmetric or antisymmetric. The proof depends on the fact that the Hamiltonian  $H(\mathbf{x}_1, \mathbf{x}_2)$  is symmetric, this follows\* from the fact that electrons are indistinguishable particles. We first consider an energy  $E = E_0$  such that (40) has nondegenerate solutions  $\psi_0$ . This means that if  $\psi_0$  and  $\psi_0'$  are any two solutions of  $(H - E_0)\psi = 0$  then  $\psi_0' = a\psi_0$  where  $a$  is a constant. It will be shown later that the ground state of the He atom is an example of such a nondegenerate state.  $H$  being symmetric,  $\psi_0(\mathbf{x}_2, \mathbf{x}_1)$  will be a solution of  $(H - E_0)\psi = 0$  if  $\psi_0(\mathbf{x}_1, \mathbf{x}_2)$  is a solution, and therefore  $\psi_0(\mathbf{x}_2, \mathbf{x}_1) = a\psi_0(\mathbf{x}_1, \mathbf{x}_2)$ . But interchange of coordinates does not change the normalization of the function and therefore  $|a|^2 = 1$  and  $a = e^{i\delta}$  with  $\delta$  real. The effect of interchanging coordinates is thus to multiply the function by a phase factor,

$$\psi_0(\mathbf{x}_2, \mathbf{x}_1) = e^{i\delta}\psi_0(\mathbf{x}_1, \mathbf{x}_2).$$

Interchanging twice we have

$$\psi_0(\mathbf{x}_2, \mathbf{x}_1) = e^{i\delta}\psi_0(\mathbf{x}_1, \mathbf{x}_2) = e^{2i\delta}\psi_0(\mathbf{x}_2, \mathbf{x}_1)$$

so that  $e^{2i\delta} = 1$  and  $e^{i\delta} = \pm 1$ . This proves that  $\psi_0(\mathbf{x}_2, \mathbf{x}_1) = \pm \psi_0(\mathbf{x}_1, \mathbf{x}_2)$  for nondegenerate states. Now let us suppose that the atom is brought into some other state, which may belong to a degenerate energy level, by an external perturbation. Before the perturbation is turned on the complete time-dependent wave function will be  $\psi_0(\mathbf{x}_1, \mathbf{x}_2, t) = \psi_0(\mathbf{x}_1, \mathbf{x}_2) \exp(-iE_0 t/\hbar)$

\* The symmetry of  $H$  is obvious for the electrostatic Hamiltonian in (9)

and during the transition the complete wave function will be a solution of the time-dependent Schrödinger equation

$$H(\mathbf{x}_1, \mathbf{x}_2, t)\psi(\mathbf{x}_1, \mathbf{x}_2, t) = i\hbar \frac{\partial}{\partial t} \psi(\mathbf{x}_1, \mathbf{x}_2, t).$$

But since  $H(\mathbf{x}_1, \mathbf{x}_2, t)$  is always a symmetric function of  $\mathbf{x}_1, \mathbf{x}_2$  any function  $\psi$  which is originally symmetric will always remain symmetric, and any function which is originally antisymmetric will always remain antisymmetric. We may therefore conclude that all wave functions for many-electron systems must be either symmetric or antisymmetric for interchange of the coordinates of any pair of electrons. It is readily shown that the physical properties associated with symmetric wave functions are different from those associated with antisymmetric wave functions, and since we do not observe different types of pairs of negative electrons it may be concluded that only symmetric, or antisymmetric, electron states occur in nature. The Pauli principle allows us to choose between these two possibilities. The requirement that  $H$  be symmetric imposes the condition that the central field potentials  $v_1, v_2$  be identical. A symmetrical solution for the two-electron central field problem is

$$\varphi(\alpha_1|\mathbf{x}_1)\varphi(\alpha_2|\mathbf{x}_2) + \varphi(\alpha_1|\mathbf{x}_2)\varphi(\alpha_2|\mathbf{x}_1)$$

and an antisymmetric solution is

$$\varphi(\alpha_1|\mathbf{x}_1)\varphi(\alpha_2|\mathbf{x}_2) - \varphi(\alpha_1|\mathbf{x}_2)\varphi(\alpha_2|\mathbf{x}_1). \quad (37)$$

The antisymmetric solution vanishes if  $\alpha_1 = \alpha_2$ . We therefore conclude that *only antisymmetric electron states occur in nature*. The Pauli principle is then satisfied automatically.

Henceforth, following Condon and Shortley, we shall adopt the convention of using capital  $\Psi$  only for antisymmetric functions.

## 5.2 Antisymmetrical Functions for $N$ Electrons

Suppose that we are given a set of one-electron orbitals  $\varphi(\alpha_1|\mathbf{x}_1), \varphi(\alpha_2|\mathbf{x}_2), \dots, \varphi(\alpha_N|\mathbf{x}_N)$ . We may then obtain the functions

$$D(A|X) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi(\alpha_1|\mathbf{x}_1) & \varphi(\alpha_2|\mathbf{x}_1) \dots \varphi(\alpha_N|\mathbf{x}_1) \\ \varphi(\alpha_1|\mathbf{x}_2) & \varphi(\alpha_2|\mathbf{x}_2) \dots \varphi(\alpha_N|\mathbf{x}_2) \\ \vdots & \vdots \\ \varphi(\alpha_1|\mathbf{x}_N) & \varphi(\alpha_2|\mathbf{x}_N) \dots \varphi(\alpha_N|\mathbf{x}_N) \end{vmatrix} \quad (41)$$

where  $A$  is written for the set of quantum numbers  $(\alpha_1, \alpha_2, \dots, \alpha_N)$  and  $X$  for the set of coordinates  $(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ . Functions of the type (41) will be

termed *D functions*. Since the effect of interchanging any two rows is to multiply a determinant by  $-1$ , a *D* function will be an antisymmetric function of the coordinates.

Since a determinant vanishes if two columns are identical,  $D(A|X) = 0$  if  $\alpha_i = \alpha_j$  for any  $i \neq j$ . For *D* to be nonzero the quantum numbers *A* must therefore be consistent with the Pauli principle. The transformation  $\varphi(\alpha_i) \rightarrow \varphi(\alpha_i) + c\varphi(\alpha_j)$  leaves  $D(A|X)$  unchanged. Transformation of this type may therefore be made in such a way that  $(\alpha_i|\alpha_j) = 0$  for all  $i \neq j$ . We may also take the orbitals to be normalized. We then have

$$(\alpha_i|\alpha_j) = \delta_{ij}. \quad (42)$$

In § 10.2 it will be shown that  $D(A|X)$  will be normalized to unity when (42) is satisfied for all  $i, j$

### 5.3 Parity

A function  $f(\mathbf{r}_1, \mathbf{r}_2, \dots)$  is said to be of *even parity* if  $f(\mathbf{r}_1, \mathbf{r}_2, \dots) = +f(-\mathbf{r}_1, -\mathbf{r}_2, \dots)$  and of *odd parity* if  $f(\mathbf{r}_1, \mathbf{r}_2, \dots) = -f(-\mathbf{r}_1, -\mathbf{r}_2, \dots)$ . Since the Hamiltonian for an atom is of even parity it follows by an argument similar to that of § 5.1 that the wave function must be either of even or of odd parity. However, the Hamiltonian for an external perturbation of an atom may be of even or of odd parity (for example, an external constant electric field will be a perturbation of odd parity). We may therefore expect to find atomic states of even and of odd parity

Any matrix element

$$(\alpha|P|\beta) = \int \psi_\alpha^* P \psi_\beta d\mathbf{x}$$

will be zero unless the entire integrand,  $\psi_\alpha^* P \psi_\beta$ , is of even parity. Therefore, if *P* is of even parity  $(\alpha|P|\beta)$  will be zero if  $\psi_\alpha^*, \psi_\beta$  have different parities; if *P* is of odd parity  $(\alpha|P|\beta)$  will be zero if  $\psi_\alpha^*, \psi_\beta$  are of the same parity.

The transformation  $\mathbf{r} \rightarrow -\mathbf{r}$  corresponds to  $\theta \rightarrow (\pi - \theta)$  and  $\varphi \rightarrow (\pi + \varphi)$ . From (20) and the definition of the associated Legendre polynomials<sup>17</sup> one may obtain

$$Y_{lm_l}(\hat{\mathbf{r}}) = (-1)^{l_l} Y_{lm_l}(-\hat{\mathbf{r}}).$$

Central field wave functions belonging to a configuration  $n_1 l_1 n_2 l_2 \dots n_N l_N$  will therefore be of even parity if  $(l_1 + l_2 + \dots + l_N)$  is even, and of odd parity if  $(l_1 + l_2 + \dots + l_N)$  is odd. The parity of atomic wave functions may therefore be determined if it is possible to make a one-to-one

correspondence between the exact functions and the wave functions of a central field model.

## 6. Perturbation Procedures

### 6.1 The Central Field Model and the Exact Electrostatic Hamiltonian

Suppose that we have a central field Hamiltonian

$$H^{\text{cf}} = \sum_i \left[ -\frac{\hbar^2}{2m} \nabla_i^2 + v(r_i) \right]$$

and that we have obtained solutions  $\Psi(\Gamma)$  of the central field Schrödinger equation

$$[H^{\text{cf}} - E_\Gamma^{\text{cf}}] \Psi(\Gamma) = 0.$$

We take  $\Psi$  to be antisymmetric for interchange of all coordinate pairs.

We wish to estimate the energy levels  $E_\Gamma$  for the exact electrostatic Hamiltonian

$$H = \sum_i \left[ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} \right] + \sum_{i,j} e^2 \quad (44)$$

We first calculate the matrix elements

$$(\Gamma|H|\Gamma') = \int \Psi^*(\Gamma) H \Psi(\Gamma') d\tau.$$

The required energy levels are then obtained on solving the *secular equation* (see Vol. I, Chapter 5, § 3.1.)

$$\det |(\Gamma|H|\Gamma') - E \delta_{\Gamma\Gamma'}| = 0, \quad (45)$$

that is,

$$\begin{vmatrix} (1|H|1) - E & (1|H|2) & (1|H|3) \dots \\ (2|H|1) & (2|H|2) - E & (2|H|3) \dots \\ \vdots & \vdots & \ddots \end{vmatrix} = 0. \quad (46)$$

Let  $E = E_\Gamma$  be a solution of (46). If  $(E_\Gamma - E_\Gamma^{\text{cf}})$  is not too large one may obtain approximate solutions using perturbation theory.

One must allow for the fact that the central field levels are usually *degenerate*; the central field energies depend only on the configuration and for a given configuration there will be a number of linearly independent



functions  $\Psi(\Gamma)$ . The first step in applying perturbation theory is to choose functions  $\Psi(\Gamma)$  to be such that

$$(\Gamma|H|\Gamma') = 0 \quad (47)$$

for  $\Gamma \neq \Gamma'$  but  $\Gamma, \Gamma'$  belonging to the same configuration. Assuming (47) to be satisfied, first-order perturbation theory gives

$$E_r = (\Gamma|H|\Gamma) \quad (48)$$

and second-order perturbation theory gives

$$E_r = (\Gamma|H|\Gamma) + \sum_{\Gamma''}'' \frac{|(\Gamma|H|\Gamma'')|^2}{(E_r^{\text{cf}} - E_{\Gamma''}^{\text{cf}})} \quad (49)$$

where the sum  $\Sigma''$  is over all states  $\Gamma''$  belonging to configurations different from the configuration of  $\Gamma$ .

The condition (47) is that the matrix of  $H$  should be diagonal for all states within a given configuration. If we choose  $\Gamma$  to stand for the quantum numbers

$$(n_1 l_1 m_{l_1} m_{s_1}, n_2 l_2 m_{l_2} m_{s_2}, \dots, n_N l_N m_{l_N} m_{s_N}) \quad (50)$$

this condition will not, in general, be satisfied. We may, however, choose states which are linear combinations of the states with representation (50) and we may do this in such a way that (47) will be satisfied. In order to develop a systematic procedure we require two theorems on commuting operators.

## 6.2 Commuting Operators

Let  $A$  be an operator with eigenvalues  $a$ ,  $B$  an operator with eigenvalues  $b$  and let  $A$  and  $B$  commute:  $AB - BA = 0$ .

*Theorem I* states that there exists a set of simultaneous eigenstates  $\psi(ab)$  of  $A$  and  $B$ . (Vol. I, Chapter 2, § 3.3.).

*Theorem II* states that the matrix element  $(a|B|a')$  is zero if  $a$  is not equal to  $a'$ . (This follows from  $(a|AB - BA|a') = (a - a')(a|B|a')$  being zero since  $AB = BA$ .)

Suppose that we can find a set of functions  $\Psi(\Gamma)$  with

$$\Gamma = (\gamma, a_1, a_2, \dots, a_p) \quad (51)$$

where  $\gamma$  specifies a configuration and where  $a_1, a_2, \dots, a_p$  are the eigenvalues of a set of commuting operators  $A_1, A_2, \dots, A_p$  all of which commute with  $H$ . Suppose furthermore that no two states belonging to the same configura-

tions have the same set of eigenvalues  $a_1, a_2, \dots, a_p$ . It follows that the set of functions  $\Psi(I')$  will satisfy the condition (47).

The operators  $A_1, A_2, \dots, A_p$  correspond to the constants of motion which would be introduced in the course of solving a problem in classical dynamics. The most important of such operators are those for the total angular momenta.

## 7. The Quantum Theory of Angular Momentum

### 7.1 Angular Momentum Operators

The classical orbital angular momentum of a particle is  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ ,  $\mathbf{p}$  being the linear momentum. The Cartesian components of  $\mathbf{L}$  are

$$\begin{aligned} L_x &= y\dot{p}_z - z\dot{p}_y, \\ L_y &= z\dot{p}_x - x\dot{p}_z, \\ L_z &= x\dot{p}_y - y\dot{p}_x. \end{aligned} \quad (52)$$

The quantum mechanical orbital angular momentum operator is obtained on taking for  $\mathbf{p}$  the operator  $\mathbf{p} = -i\hbar\nabla$ . Using commutation relations of the type

$$x\dot{p}_x - \dot{p}_x x = i\hbar, \quad x\dot{p}_y - \dot{p}_y x = 0,$$

one obtains the commutation relations satisfied by the orbital angular momentum components,

$$\begin{aligned} L_x L_y - L_y L_x &= i\hbar L_z, \\ L_y L_z - L_z L_y &= i\hbar L_x, \\ L_z L_x - L_x L_z &= i\hbar L_y. \end{aligned}$$

The general definition of an angular momentum operator is that  $\mathbf{J}$  is such an operator if the components of  $\mathbf{J}$  satisfy

$$\begin{aligned} J_x J_y - J_y J_x &= i\hbar J_z, \\ J_y J_z - J_z J_y &= i\hbar J_x, \\ J_z J_x - J_x J_z &= i\hbar J_y. \end{aligned} \quad (53)$$

Since the components  $J_x, J_y, J_z$  do not commute among themselves we cannot form simultaneous eigenfunctions of the components. Defining

$$\mathbf{J}^2 = J_x^2 + J_y^2 + J_z^2 \quad (54)$$

it is readily shown that  $\mathbf{J}^2$  commutes with the components  $J_x, J_y$  and  $J_z$ . We may therefore obtain simultaneous eigenfunctions of  $\mathbf{J}^2$  and of any one component, conventionally chosen to be  $J_z$ . Using only the commutation relations (53) it may be shown<sup>8, 9, 11</sup> that the simultaneous eigenfunctions  $\varphi(jm)$  satisfy

$$\mathbf{J}^2 \varphi(jm) = \hbar^2 j(j+1) \varphi(jm) \quad (55)$$

$$J_z \varphi(jm) = \hbar m \varphi(jm) \quad (56)$$

with  $j = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots$  and, for given  $j$ ,

$$m = j, (j-1), \dots, (-j). \quad (57)$$

With the more restricted definition (52) of orbital angular momentum we would have obtained  $j = l$  with  $l$  an integer. The definition of  $\mathbf{J}$  in terms of commutation relations includes the case of spin angular momentum  $\mathbf{J} = \mathbf{S}$ ,  $j = s = \frac{1}{2}$ ,  $m = m_s = \pm \frac{1}{2}$ .

## 7.2 The Operator $J_-$

Introducing

$$J_- = J_x - iJ_y \quad (58)$$

we obtain from the commutation relations

$$J_z J_- = J_- (J_z - \hbar). \quad (59)$$

Therefore, using (56),

$$J_z [J_- \varphi(jm)] = \hbar(m-1) [J_- \varphi(jm)].$$

Since  $J_-$  commutes with  $\mathbf{J}^2$  we also have

$$J^2 [J_- \varphi(jm)] = J_- J^2 \varphi(jm) = \hbar^2 j(j+1) [J_- \varphi(jm)].$$

The equations satisfied by  $[J_- \varphi(jm)]$  are therefore identical with those satisfied by  $\varphi(jm-1)$ , and it follows that  $[J_- \varphi(jm)]$  must be proportional to  $\varphi(jm-1)$ , that is,

$$J_- \varphi(jm) = \mathcal{N}(jm) \varphi(jm-1).$$

The proportionality constant may be obtained from the normalization condition  $\int |\varphi(jm-1)|^2 d\tau = 1$ . This gives

$$|\mathcal{N}(jm)|^2 = \int [J_- \varphi(jm)]^* J_- \varphi(jm) d\tau.$$

Since  $\mathbf{J}$  is Hermitian we have\*

$$\int [J_x u]^* v \, d\tau = \int u^* J_x v \, d\tau$$

and similar relations for  $J_y$  and  $J_z$ . Therefore

$$|\mathcal{N}(jm)|^2 = \int \varphi^*(jm)(J_x + iJ_y)(J_x - iJ_y)\varphi(jm) \, d\tau.$$

Using the commutation relations (53) one obtains

$$(J_x + iJ_y)(J_x - iJ_y) = J^2 - J_z^2 + \hbar J_z$$

and therefore

$$|\mathcal{N}(jm)|^2 = \hbar^2[j(j+1) - m^2 + m] = \hbar^2(j+m)(j-m+1)$$

The phase of  $\mathcal{N}(jm)$  depends on the relative phases of the states  $\varphi(jm)$  for different values of  $m$ . We adopt the conventional choice for which

$$\mathcal{N}(jm) = \hbar[j(j+m)(j-m+1)]^{1/2} \quad (60)$$

It was this convention which led to the phase choice for the spherical harmonics defined by (20).

### 7.3 Angular Momentum Coupling

Let  $\mathbf{J}_1, \mathbf{J}_2$  be two commuting angular momenta, these could, for example, be the individual orbital angular momenta for two electrons, or they could be the orbital and spin angular momenta for a single electron. The total angular momentum operator is defined by

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2, \quad J_z = J_{1z} + J_{2z} \quad (61)$$

Using the commutation relations for the components of  $J_1$  and  $J_2$ , and the fact that  $J_1, J_2$  commute it is readily shown that the components of  $\mathbf{J}$  satisfy the commutation relations for an angular momentum operator. It is also readily shown that a set of commuting operators is provided by  $\mathbf{J}_1^2, \mathbf{J}_2^2, \mathbf{J}^2$ , and  $J_z$ . These operators will therefore have simultaneous eigenfunctions  $\psi(j_1, j_2, j, m)$  where  $j_1, j_2, j$ , and  $m$  are the quantum numbers for  $\mathbf{J}_1^2, \mathbf{J}_2^2, \mathbf{J}^2$  and  $J_z$ .

\* It should be noted that  $J_-$ , which does not correspond to an observable quantity, is not Hermitian

Since the functions

$$\varphi(j_1 j_2 m_1 m_2) = \varphi(j_1 m_1) \varphi(j_2 m_2)$$

form a complete set, an expansion of the type

$$\psi(j_1 j_2 j m) = \sum_{m_1, m_2} (j_1 j_2 m_1 m_2 | j_1 j_2 j m) \varphi(j_1 j_2 m_1 m_2) \quad (62)$$

must exist. The coefficients  $(j_1 j_2 m_1 m_2 | j_1 j_2 j m)$  are termed vector-coupling, Wigner, or Clebsch-Gordan coefficients.

Operating on (62) with  $J_z = J_{1z} + J_{2z}$  shows that the coefficients will be zero unless  $m_1 + m_2 = m$ . For given  $j_1, j_2$  the largest value of  $m_1$  is  $m_1 = j_1$  and the largest value of  $m_2$  is  $m_2 = j_2$ . The largest value of  $m$  which can occur in  $\psi(j_1 j_2 j m)$  is therefore  $m = j_1 + j_2$ . Since  $\mathbf{J}$  is an angular momentum operator it follows that, for each value of  $j$ , there must exist the  $(2j + 1)$  values of  $m$  given by (57). Therefore  $j = j_1 + j_2$  is the largest value of  $j$  which can occur. In the expansion of  $\psi(j_1 j_2 j_1 + j_2 j_1 + j_2)$  there is only one term on the right-hand side. Making the conventional phase choice we have

$$\psi(j_1 j_2 j_1 + j_2 j_1 + j_2) = \varphi(j_1 j_2 j_1 j_2).$$

For  $m = j_1 + j_2 - 1$  there are two functions on the right-hand side of (62),  $\varphi(j_1 j_2 j_1 j_2 - 1)$  and  $\varphi(j_2 j_1 - 1 j_2)$ . There are therefore two linearly independent functions  $\psi$  with  $m = j_1 + j_2 - 1$ . One of these has  $j = j_1 + j_2$ , and the other must have  $j = j_1 + j_2 - 1$ . Continuing a similar argument it may be shown that the allowed values of  $j$  are

$$j = (j_1 + j_2), (j_1 + j_2 - 1), \dots, |j_1 - j_2|. \quad (63)$$

#### 7.4 Calculation of Vector-Coupling Coefficients for $j_1 = j_2 = 1$

When the quantum numbers  $j_1, j_2$  are understood we write

$$\psi(j_1 j_2 j m) = \psi(j m) \quad \text{and} \quad \varphi(j_1 j_2 m_1 m_2) = \varphi(m_1 m_2).$$

We proceed to calculate the coupled eigenfunctions for  $j_1 = j_2 = 1$ . For  $j = m = 2$  we have  $\psi(2 2) = \varphi(1 1)$ . Operating with  $J_- = J_{1-} + J_{2-}$ , we have

$$\begin{aligned} J_- \psi(j m) &= \mathcal{N}(j m) \psi(j m - 1) \\ J_{1-} \varphi(m_1 m_2) &= \mathcal{N}(1 m_1) \varphi(m_1 - 1 m_2) \\ J_{2-} \varphi(m_1 m_2) &= \mathcal{N}(1 m_2) \varphi(m_1 m_2 - 1). \end{aligned}$$

Operating on  $\psi(2\ 2)$  we have

$$\mathcal{N}(22)\psi(21) = \mathcal{N}(11)\varphi(01) + \mathcal{N}(11)\varphi(10).$$

From (60),  $\mathcal{N}(2\ 2) = 2\hbar$  and  $\mathcal{N}(1\ 1) = \sqrt{2}\hbar$ . Therefore

$$\psi(21) = \frac{1}{\sqrt{2}}\{\varphi(01) + \varphi(10)\}.$$

By continued operation with  $J_-$  all states  $\psi(2m)$  may be obtained.

Collecting results\* we have

$m$	$\psi(2m)$	
$2$	$\varphi(11)$	
$1$	$(1/\sqrt{2})[\varphi(01) + \varphi(10)]$	(64 a)
$0$	$(1/\sqrt{6})[\varphi(11) + 2\varphi(00) + \varphi(1\bar{1})]$	
$\bar{1}$	$(1/\sqrt{2})[\varphi(10) + \varphi(0\bar{1})]$	
$\bar{2}$	$\varphi(\bar{1}\bar{1})$ .	

We now consider  $l = 1$ . We know that  $\psi(11)$  must be a linear combination of  $\varphi(01)$  and  $\varphi(10)$ , that is,

$$\psi(11) = a\varphi(01) + b\varphi(10).$$

Since  $\psi(11)$  should be orthogonal to  $\psi(21)$  and should be normalized, we obtain  $a + b = 0$  and  $|a|^2 + |b|^2 = 1$ . Therefore

$$\psi(11) = (e^{i\delta}/\sqrt{2})[\varphi(01) - \varphi(10)],$$

the phase  $\delta$  being arbitrary. The conventional choice† is to take  $e^{i\delta} = -1$ . All states  $\psi(1m)$  may be obtained from  $\psi(11)$  using the operator  $J_-$ . This gives

$m$	$\psi(1m)$	
$1$	$(1/\sqrt{2})[-\varphi(01) + \varphi(10)]$	
$0$	$(1/\sqrt{2})[-\varphi(11) + \varphi(1\bar{1})]$	(64 b)
$\bar{1}$	$(1/\sqrt{2})[-\varphi(10) + \varphi(0\bar{1})]$ .	

\* We write  $\bar{1}$  for  $-1$  etc.

† Condon and Shortley,<sup>8</sup> p. 66; Edmonds,<sup>8</sup> p. 37.

Finally  $\psi(00)$  is determined at it should be a linear combination of  $\varphi(\bar{1}1)$ ,  $\varphi(00)$  and  $\varphi(1\bar{1})$ , that it be orthogonal to  $\psi(20)$  and  $\psi(10)$ , and that it be normalized. With the conventional phase choice we obtain

$$\psi(00) = (1/\sqrt{3})[\varphi(\bar{1}1) - \varphi(00) + \varphi(1\bar{1})]. \quad (64 c)$$

### 7.5 Coupling Coefficients for $j_1 = j_2 = \frac{1}{2}$

It is left as an exercise for the reader to show that, for  $j_1 = j_2 = \frac{1}{2}$ ,

$$\begin{aligned} \psi(11) &= \varphi(\tfrac{1}{2} \tfrac{1}{2}) \\ \psi(10) &= (1/\sqrt{2}) [\varphi(\tfrac{1}{2} \tfrac{1}{2}) + \varphi(\tfrac{1}{2} \tfrac{1}{2})] \\ \psi(1\bar{1}) &= \varphi(\tfrac{1}{2} \tfrac{1}{2}) \end{aligned} \quad (65 a)$$

and

$$\psi(00) = (1/\sqrt{2}) [-\varphi(\tfrac{1}{2} \tfrac{1}{2}) + \varphi(\tfrac{1}{2} \tfrac{1}{2})]. \quad (65 b)$$

### 7.6 Properties of the Coupling Coefficients

The method of § 7.4. may be generalized<sup>7-9</sup> and after some lengthy algebra an explicit expression for the coupling coefficients may be obtained. The explicit expression is cumbersome and will not be quoted. Condon and Shortley<sup>8</sup> give tables which are sufficient for most atomic structure applications.

With the usual phase conventions the coupling coefficients are real. From the fact that the coupled eigenfunctions (62) form a complete orthonormal set one obtains the unitary relations

$$\sum_{m_1 m_2} (j_1 j_2 m_1 m_2 | j_1 j_2 j m) (j_1 j_2 m_1 m_2 | j_1 j_2 j' m') = \delta_{j j'} \delta_{m m'} \quad (66)$$

The inverse of the transformation (62) is

$$\varphi(j_1 j_2 m_1 m_2) = \sum_{j m} (j_1 j_2 j m | j_1 j_2 m_1 m_2) \psi(j_1 j_2 j m) \quad (67)$$

where

$$(j_1 j_2 j m | j_1 j_2 m_1 m_2) = (j_1 j_2 m_1 m_2 | j_1 j_2 j m).$$

From (67) one obtains

$$\sum_{j m} (j_1 j_2 j m | j_1 j_2 m_1 m_2) (j_1 j_2 j m | j_1 j_2 m'_1 m'_2) = \delta_{m_1 m'_1} \delta_{m_2 m'_2} \quad (68)$$

### 7.7 Symmetry Properties of Coupled Eigenfunctions for $j_1 = j_2$

Consider the coupling of two spin angular momenta. With the representation of § 2.5. for the individual spin functions we have, from (65 a and b),

$$\begin{array}{ll}
 SM_S & \psi(\frac{1}{2} \frac{1}{2} SM_S | \sigma_1, \sigma_2) \\
 11 & \delta(\frac{1}{2} | \sigma_1) \delta(\frac{1}{2} | \sigma_2) \\
 10 & (1/\sqrt{2}) [\delta(\frac{1}{2} | \sigma_1) \delta(\frac{1}{2} | \sigma_2) + \delta(\frac{1}{2} | \sigma_1) \delta(\frac{1}{2} | \sigma_2)] \\
 1\bar{1} & \delta(\frac{1}{2} | \sigma_1) \delta(\frac{1}{2} | \sigma_2) \\
 00 & (1/\sqrt{2}) [-\delta(\frac{1}{2} | \sigma_1) \delta(\frac{1}{2} | \sigma_2) + \delta(\frac{1}{2} | \sigma_1) \delta(\frac{1}{2} | \sigma_2)].
 \end{array}$$

It is seen that  $\psi(\frac{1}{2} \frac{1}{2} SM_S | \sigma_1, \sigma_2)$  is a symmetric function of  $\sigma_1, \sigma_2$  for  $S = 1$  and an antisymmetric function for  $S = 0$ .

Consider in the same way the coupling of two orbital angular momenta with  $l_1 = l_2 = 1$ . From the results of § 7.4. we obtain

$$\begin{array}{ll}
 LM_L & \psi(11LM_L | \hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \\
 22 & Y_{11}(\hat{\mathbf{r}}_1) Y_{11}(\hat{\mathbf{r}}_2) \\
 11 & (1/\sqrt{2}) [-Y_{10}(\hat{\mathbf{r}}_1) Y_{11}(\hat{\mathbf{r}}_2) + Y_{11}(\hat{\mathbf{r}}_1) Y_{10}(\hat{\mathbf{r}}_2)] \\
 00 & (1/\sqrt{3}) [Y_{11}(\hat{\mathbf{r}}_1) Y_{11}(\hat{\mathbf{r}}_2) - Y_{10}(\hat{\mathbf{r}}_1) Y_{10}(\hat{\mathbf{r}}_2) + Y_{11}(\hat{\mathbf{r}}_1) Y_{11}(\hat{\mathbf{r}}_2)].
 \end{array}$$

The functions  $\psi(11LM_L | \hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$  are seen to be symmetric for  $L = 2$ , antisymmetric for  $L = 1$ , and symmetric for  $L = 0$ .

These results may be shown to be special cases of a more general theorem:  $\psi(j_1 j_2 jm)$  is symmetric if  $(2j_1 - j)$  is even, and is antisymmetric if  $(2j_1 - j)$  is odd.

### 7.8 Scalar Operators

Let  $A$  be any operator and let  $J$  be an angular momentum operator. It may be shown<sup>8,9,11,22</sup> that the commutation relations satisfied by  $A$  and  $J$  define the behaviour of  $A$  when the coordinate system is rotated. An operator  $P$  is said to be a scalar if it commutes with  $J$ . By theorem I of § 6.2. one may obtain simultaneous eigenfunctions  $\psi(pjm)$  of  $\mathbf{J}^2, J_z$  and a scalar  $P$ . Let  $Q$  be a second scalar operator. By theorem II of § 6.2. the matrix elements  $\langle pj m | Q | p' j' m' \rangle$  will be zero for  $(jm) \neq (j'm')$ . We now show\* that  $\langle pj m | Q | p' j' m \rangle$  is independent of  $m$ .

\* This proof is given by Condon and Shortley,<sup>8</sup> p. 49.



We have

$$Q\psi(p'jm) = \sum (pjm|Q|p'jm)\psi(pjm)$$

and therefore

$$J_- Q\psi(p'jm) = \sum_p (pjm|Q|p'jm) \mathcal{N}(jm)\psi(pjm-1). \quad (69)$$

But

$$J_- \psi(p'jm) = \mathcal{N}(jm)\psi(p'jm-1)$$

and therefore

$$QJ_- \psi(p'jm) = \mathcal{N}(jm) \sum_p (pjm-1|Q|p'jm-1)\psi(pjm-1). \quad (70)$$

Since  $J_- Q = QJ_-$ , (69) and (70) are equal and equating coefficients of  $\psi(pjm-1)$  gives

$$(pjm|Q|p'jm) = (pjm-1|Q|p'jm-1).$$

This completes the proof.

In the absence of external fields the Hamiltonian for an atom will commute with the total angular momentum  $\mathbf{J}$  and the energy will therefore not depend on the quantum number  $M_J$ . This tells us, in effect, that the energy does not depend on the orientation of the atom.

## 8. Coupling Schemes for Electron Wave Functions

### 8.1 Coupling Schemes for One-Electron Problems

In order to illustrate the application of the ideas developed in the two preceding sections we consider the one-electron problem with Hamiltonian

$$H = H^{\text{cf}} + H_{\text{sp}} + H_{\text{mag}}.$$

Where  $H^{\text{cf}}$  is a central field Hamiltonian,  $H_{\text{sp}} = \xi(r)\mathbf{S} \cdot \mathbf{L}$  is the spin-orbit Hamiltonian and  $H_{\text{mag}} = (eH/2mc)(L_z + 2S_z)$  is the Hamiltonian for interaction with an external magnetic field.

Consider first the case  $H_{\text{sp}} = H_{\text{mag}} = 0$ . The fact that  $H$  commutes with  $\mathbf{S}^2, S_z, \mathbf{L}^2$  and  $L_z$  provides a formal justification for the use of the simultaneous eigenfunctions  $\varphi(nlm, m_s)$ . The fact that the energy depends

only on  $nl$  is a consequence of the theorem of § 7.8. Since  $H$  also commutes with  $S^2, L^2, J^2$  and  $J_z$ , we could equally well use the functions  $\varphi(nljm_j)$ .

We now allow for  $H_{sp}$  and  $H_{mag}$  assuming that both are small compared with the energy differences between the unperturbed  $nl$  levels. We need therefore consider only those functions  $\varphi$  belonging to a given  $nl$ . It may be shown that  $H_{sp}$  commutes with  $S^2, L^2, J^2$  and  $J_z$ , but does not commute with  $S_z$  and  $L_z$ . In order that the matrix of  $H_{sp}$  should be diagonal it is therefore necessary to use the functions  $\varphi(nljm_j)$ . Since  $S \cdot L = \frac{1}{2}(J^2 - S^2 - L^2)$  we obtain for the diagonal elements

$$(nljm_j|H_{sp}|nljm_j) = \frac{1}{2}[\gamma(\gamma + 1) - \frac{1}{2}(\frac{1}{2} + 1) - l(l + 1)]\zeta(nl)$$

in agreement with the results of § 3.5. Turning our attention to the external magnetic contribution, we find that  $H_{mag}$  commutes with  $L^2, L_z, S^2$  and  $S_z$ , but that it does not commute with  $J^2$ . To obtain a diagonal matrix for  $H_{mag}$  it is therefore necessary to use the functions  $\varphi(nlm_l m_s)$ . The diagonal elements are

$$(nlm_l m_s|H_{mag}|nlm_l m_s) = \frac{eH}{2mc} (m_l + 2m_s)\hbar.$$

The position is thus seen to be that neither of the two representations,  $(nlm_l m_s)$  or  $(nljm_j)$ , will diagonalize the complete energy matrix

In the weak field case (Zeeman effect,  $H_{mag} \ll H_{sp}$ ) we use the representation  $(nljm_j)$  and neglect the off-diagonal elements of  $H_{mag}$ . Use of second-order perturbation theory shows that the error will be proportional to the square of the neglected terms (compare § 6.1.). Calculation of the diagonal matrix elements gives\*

$$(nljm_j|H_{mag}|nljm_j) = \frac{eH}{2mc} \left[ 1 + \frac{[\frac{1}{2}(\frac{1}{2} + 1) + j(j + 1) - l(l + 1)]}{2j(j + 1)} \right] m_j \hbar$$

in agreement with the result deduced by a physical argument in § 3.6.

In the strong field case (Paschen-Back effect,  $H_{mag} \gg H_{sp}$ ) one uses the functions  $\varphi(nlm_l m_s)$  and neglects the off-diagonal matrix elements of  $H_{sp}$ . It may be shown† that the diagonal elements of  $H_{sp}$  are

$$(nlm_l m_s|H_{sp}|nlm_l m_s) = m_s m_l \zeta(nl)$$

in agreement with the result deduced in § 3.7.

\* This calculation is described by Condon and Shortley,<sup>3</sup> p. 380, and by Edmonds,<sup>4</sup> p. 112.

† Condon and Shortley,<sup>3</sup> p. 58.

For field strengths intermediate between the limiting cases of the Zeeman effect and the Paschen-Back effect it is necessary to choose one or other of the two representations and to calculate the entire energy matrix including all off-diagonal elements. The energies are then obtained on solving the secular equation (compare (46)).

## 8.2 Many-Electron Systems: $LS$ and $jj$ Coupling

We introduce the total spin and total orbital angular momenta,

$$\mathbf{S} = \sum \mathbf{S}_i, \quad \mathbf{L} = \sum \mathbf{L}_i$$

One may show that the exact electrostatic Hamiltonian (44) commutes with  $\mathbf{L}^2, \mathbf{L}_z, \mathbf{S}^2$  and  $S_z$ . We therefore introduce functions  $\Psi(\gamma S L M_S M_L)$  where  $S M_S$  are total spin quantum numbers and  $L M_L$  are quantum numbers for the total orbital angular momentum. The other quantum numbers needed to specify the states  $\Psi$  are indicated by  $\gamma$ , in many cases of practical importance the states will be completely specified if  $\gamma$  stands for the configuration. Denoting the electrostatic Hamiltonian by  $H_{el}$ , the matrix elements

$$(\gamma S L M_S M_L | H_{el} | \gamma' S' L' M'_S M'_L)$$

will be zero for  $(S L M_S M_L) \neq (S' L' M'_S M'_L)$ . It may be shown that  $H_{el}$  commutes with  $\mathbf{J}^2$  and  $J_z$  where  $\mathbf{J} = (\mathbf{S} + \mathbf{L})$  is the total angular momentum. From the fact that  $(\gamma S L M_S M_L | H_{el} | \gamma' S' L' M'_S M'_L)$  is independent of  $M_S M_L$  it follows that  $(\gamma S L J M_J | H_{el} | \gamma' S' L' J M'_J)$  is independent of  $J M_J$ . The quantum numbers  $S L$  are usually written  $^{2S+1}L$  where  $(2S+1)$  is the *multiplicity* (singlet, doublet, triplet, ... for  $S = 0, \frac{1}{2}, 1, \dots$ ). A notation similar to that of § 3.2. is used for  $L$ , the capital letters  $S, P, D, F, \dots$  being used for  $L = 0, 1, 2, 3, \dots$ . Thus  $^3P$  means  $S = 1, L = 1$  and  $^1D$  means  $S = 0, L = 2$ . When the quantum number  $J$  is introduced we write  $^{2S+1}L_J$ ; we thus have  $^3P_0, ^3P_1, ^3P_2$  and  $^1D_2$ .

A level or group of levels with quantum numbers  $^{2S+1}L$  is called a *spectral term* and the line or lines corresponding to transitions between two terms is called a *multiplet*.

The many electron spin-orbit Hamiltonian is

$$H_{sp} = \sum_i \xi(r_i) \mathbf{S}_i \cdot \mathbf{L}_i.$$

It may be shown that  $H_{sp}$  commutes with all  $\mathbf{J}_i = \mathbf{S}_i + \mathbf{L}_i$ , and with  $\mathbf{J} = \sum \mathbf{J}_i$ , but that it does not commute with  $\mathbf{S}$  and  $\mathbf{L}$ . One uses  $LS$  (Russell Saunders)

coupling when it may be assumed that the energy due to  $H_{sp}$  is small compared with the energy differences  $E(\gamma SL) - E(\gamma S'L')$  between spectral terms. The spin-orbit energy is taken to be  $(\gamma SLJ|H_{sp}|\gamma SLJ)$ , off-diagonal matrix elements  $(\gamma SLJ|H_{sp}|\gamma S'L'J')$  being neglected.

When the spin-orbit energy is very large one uses functions  $\Psi(\beta j_1 j_2 \dots j_N J M_J)$  where  $j_i$  is the quantum number for  $\mathbf{J}_i^2$ . One then obtains a diagonal matrix for  $H_{sp}$  with elements independent of  $J M_J$ . With functions  $\Psi(\beta j_1 j_2 \dots j_N J M_J)$  the electrostatic energy matrix will not be diagonal. In the  $jj$  coupling approximation, one neglects the off-diagonal elements of the electrostatic Hamiltonian and considers only

$$(\beta j_1 j_2 \dots j_N J | H_e | \beta j_1 j_2 \dots j_N J)$$

The significance of these coupling schemes will be illustrated by various examples in later sections.

## 9. The Helium Atom

For He the spin-orbit energy is very small. We shall therefore be mainly concerned with the two-electron electrostatic Hamiltonian,

$$H(\mathbf{r}_1, \mathbf{r}_2) = H_1(\mathbf{r}_1) + H_1(\mathbf{r}_2) + \frac{1}{r_{12}} \quad (71)$$

where

$$H_1(\mathbf{r}) = -\frac{1}{2} \nabla^2 - \frac{Z}{r} \quad (72)$$

and where  $Z = 2$  for He. Atomic energy units are used.

### 9.1 Separation of Space and Spin Coordinates

An antisymmetric two-electron wave function may be written as the product of a spin function times a function of spatial coordinates:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(S M_S | \sigma_1, \sigma_2) \psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2). \quad (73)$$

The total spin  $S$  is equal to 0 or 1. For  $S = 0$  (singlet states) the spin function is antisymmetric (§ 7.7) and we must therefore choose the symmetric spatial function  $\psi_+(\mathbf{r}_1, \mathbf{r}_2) = +\psi_+(\mathbf{r}_2, \mathbf{r}_1)$ , while for  $S = 1$  (triplet states) the spin function is symmetric and we choose the antisymmetric spatial functions  $\psi_-(\mathbf{r}_1, \mathbf{r}_2) = -\psi_-(\mathbf{r}_2, \mathbf{r}_1)$ .

## 9.2 The He Ground State

In § 4.2. it was shown that the He ground state has a configuration  $1s^2$ . Since the spins must be antiparallel,  $S = 0$ . A suitable spatial function is therefore

$$\psi_+(1s^2|r_1, r_2) = \varphi(1s|r_1)\varphi(1s|r_2).$$

For the energy,  $E(1s^2) = \int \psi_+^*(1s^2) H \psi_+(1s^2) d\tau$ , one obtains

$$E(1s^2) = 2I(1s) + \left( 1s1s \left| \frac{1}{r_{12}} \right| 1s1s \right)$$

where

$$I(nl) = \int \varphi^*(nl|\mathbf{r}) H_1(\mathbf{r}) \varphi(nl|\mathbf{r}) d\mathbf{r} \quad (74)$$

and where

$$\left( 1s1s \left| \frac{1}{r_{12}} \right| 1s1s \right) = \iint \varphi^*(a|\mathbf{r}_1) \varphi^*(b|\mathbf{r}_2) \frac{1}{r_{12}} \varphi(c|\mathbf{r}_1) \varphi(d|\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (75)$$

The contributions to the energy have an obvious interpretation,  $I(1s)$  represents the kinetic energy of an electron together with its potential energy in the field of the nucleus, and  $(1s1s|1/r_{12}|1s1s)$  represents the energy of electrostatic interaction between the two electrons

## 9.3 He Excited States

We may expect that the most important excited configurations will be of the type  $1snl$  in which only one electron is excited. For these the total orbital angular momentum is  $L = l$  and the problem of orbital angular momentum coupling does not arise, the introduction of total spin quantum numbers suffices to diagonalize the energy matrix within each  $1snl$  configuration. For  $nl \neq 1s$  we may have both singlet and triplet spin states.

Let us write the spatial functions as

$$\psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\varphi(\mathbf{r}_1, \mathbf{r}_2) \pm \varphi(\mathbf{r}_2, \mathbf{r}_1)] \quad (76)$$

and let  $P$  be any symmetric operator:  $P(\mathbf{r}_1, \mathbf{r}_2) = P(\mathbf{r}_2, \mathbf{r}_1)$ . We then have

$$\begin{aligned} & \int \psi_{\pm}^*(\mathbf{r}_1, \mathbf{r}_2) P \psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) d\tau \\ &= \frac{1}{\sqrt{2}} \int \varphi^*(\mathbf{r}_1, \mathbf{r}_2) P \psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) d\tau \pm \frac{1}{\sqrt{2}} \int \varphi^*(\mathbf{r}_2, \mathbf{r}_1) P \psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) d\tau. \end{aligned}$$

Since a definite integral remains unchanged if one changes the labels on the integration variables,

$$\int \varphi^*(\mathbf{r}_2, \mathbf{r}_1) P \psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) d\tau = \int \varphi^*(\mathbf{r}_1, \mathbf{r}_2) P \psi(\mathbf{r}_2, \mathbf{r}_1) d\tau.$$

Using  $\psi_{\pm}(\mathbf{r}_2, \mathbf{r}_1) = \pm \psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2)$  we obtain

$$\begin{aligned} \int \psi_{\pm}^*(\mathbf{r}_1, \mathbf{r}_2) P \psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) d\tau \\ = \sqrt{2} \int \varphi^*(\mathbf{r}_1, \mathbf{r}_2) P \psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) d\tau = \int \varphi^*(\mathbf{r}_1, \mathbf{r}_2) P [\varphi(\mathbf{r}_1, \mathbf{r}_2) \pm \varphi(\mathbf{r}_2, \mathbf{r}_1)] d\tau. \end{aligned} \quad (77)$$

We shall refer to

$$\int \varphi^*(\mathbf{r}_1, \mathbf{r}_2) P \varphi(\mathbf{r}_1, \mathbf{r}_2) d\tau$$

as a *direct integral* and to

$$\int \varphi^*(\mathbf{r}_1, \mathbf{r}_2) P \varphi(\mathbf{r}_2, \mathbf{r}_1) d\tau$$

as an *exchange integral*.

For  $1snl$  states of He we have

$$\psi_{\pm}(1snl|\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\varphi(1s|\mathbf{r}_1)\varphi(nl|\mathbf{r}_2) \pm \varphi(1s|\mathbf{r}_2)\varphi(nl|\mathbf{r}_1)]. \quad (78)$$

Assuming the functions  $\varphi$  to be normalized it is seen from (78) that  $\psi_{\pm}$  will be normalized to unity if

$$\int \varphi^*(1s|\mathbf{r})\varphi(nl|\mathbf{r}) d\mathbf{r} = 0. \quad (79)$$

This condition will be satisfied automatically for  $l \neq 0$ . We consider the case of  $l = 0$ . It is readily shown that the function  $\psi_{-}(1sns)$  is unaltered if one makes the transformation  $\varphi(ns) \rightarrow \varphi(ns) + \varphi(1s)$ . The condition (79) may therefore be imposed without imposing any additional restriction on the form of the function  $\psi_{-}(1sns)$ . For  $\psi_{+}(1sns)$  this is no longer the case. For simplicity we shall only consider cases for which (79) is satisfied. This means that we impose an additional restriction on the form of the wave functions  $\psi_{\pm}(1sns)$ .

With normalized functions the energy is

$$\begin{aligned} \int \varphi^*(1s|\mathbf{r}_1)\varphi^*(nl|\mathbf{r}_2) H \varphi(1s|\mathbf{r}_1)\varphi(nl|\mathbf{r}_2) d\tau \pm \\ \int \varphi^*(1s|\mathbf{r}_1)\varphi^*(nl|\mathbf{r}_2) H \varphi(1s|\mathbf{r}_2)\varphi(nl|\mathbf{r}_1) d\tau. \end{aligned}$$

When (79) is satisfied only the  $(1/r_{12})$  term in  $H$  gives a nonzero contribution to the exchange integral. The energy is therefore

$$I(1s) + I(nl) + \left(1snl \left| \frac{1}{r_{12}} \right| 1snl\right) \pm \left(1snl \left| \frac{1}{r_{12}} \right| nl1s\right) \quad (80)$$

the  $+$  sign going with  $S = 0$  and the  $-$  sign with  $S = 1$ . The exchange integral  $(1snl|1/r_{12}|nl1s)$  has no classical analogue. It may be shown<sup>7</sup> that this integral is positive.

### 9.4 The He Energy Level Diagram

The observed energy levels of He (Fig. 8) may be divided into two distinct groups originally termed para-helium and ortho-helium. The ground state belongs to the para-helium group. No radiative transitions occur between the two groups. The excited states give recognizable  $nl$  series essentially similar to the series observed in alkali spectra. For a given  $nl$  it is found that the ortho-helium levels are lower than the para-helium levels.

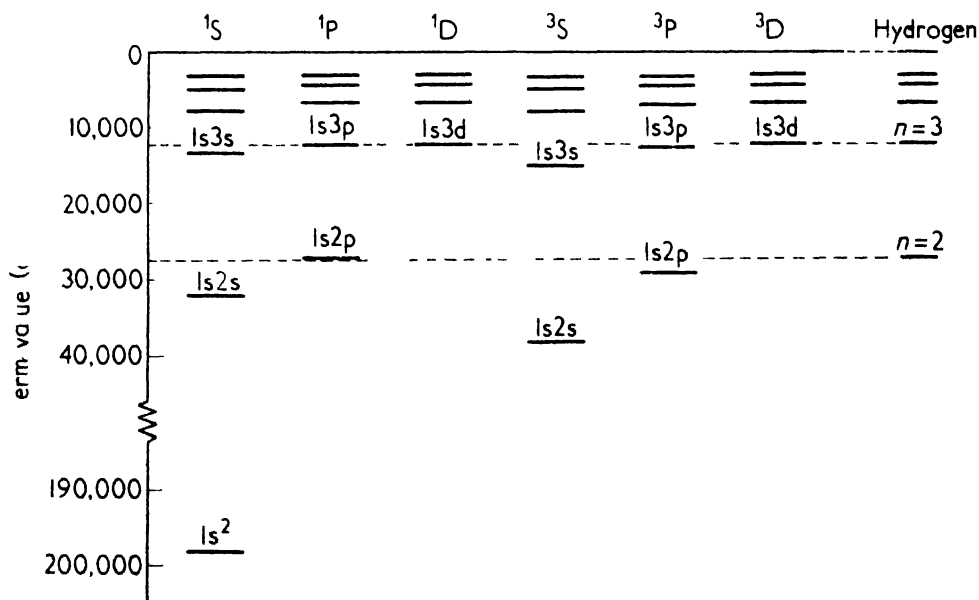


FIG. 8. S, P and D states in the He energy level diagram.

This entire picture is in complete agreement with what the theory would lead one to expect. We may identify para-helium with the singlet spin states and ortho-helium with the triplet states. The fact that the ground state belongs to the para-helium group is convincing evidence in favour

of this identification. For a given  $nl$  the energy difference between triplet and singlet states is due to the exchange integral in (80); it is this which makes the triplet (ortho-helium) levels lower than the singlet (para-helium) levels.

One interesting observation is that the term values for  $1sn p^1P$  levels are smaller than the corresponding hydrogen term values; this means that the effective charge  $Z_{np}$  in (28) will be less than unity and that the quantum defect  $\mu_{np}$  (Eq. 29) will be negative. This cannot be explained in terms of a central field model (§ 2.8.) but may be explained if the exchange energy is sufficiently large. An approximate numerical calculation will be given in § 9.6.

Observations with very high resolution show that the singlet terms have no fine structure and that the triplet terms (except  $1sns^3S$  terms) are split into three fine structure levels. This agrees with theory. However, calculation of the spin-orbit energy does not give good detailed agreement with the observed triplet fine structure. The reason for this is that the spin-orbit energy is very small and is comparable with neglected relativistic effects and with other effects such as the interactions between the two spin magnetic moments.

From the absence of radiative singlet-triplet transitions we may deduce the selection rule  $\Delta S = 0$ .

### 9.5 Reduction of Integrals

We have expressed the energies in terms of integrals defined by (74), (75). In order to evaluate these integrals the first step is to carry out the integrations over the angular coordinates. For  $I(nl)$  we obtain immediately

$$I(nl) = -\frac{1}{2} \int_0^\infty P_{nl}(r) \left[ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2Z}{r} \right] P_{nl}(r) dr. \quad (81)$$

For the reduction of  $\langle ab|1/r_{12}|cd \rangle$  we require the expansion

$$\frac{1}{r_{12}} = \sum_{\lambda} \gamma_{\lambda}(r_1, r_2) P_{\lambda}(\cos \omega) \quad (82)$$

where  $\omega$  is the angle between  $\mathbf{r}_1, \mathbf{r}_2$  and where

$$\gamma_{\lambda}(r_1, r_2) = \begin{cases} r_1^{\lambda}/r_2^{\lambda+1} & (r_1 < r_2) \\ r_2^{\lambda}/r_1^{\lambda+1} & (r_2 < r_1) \end{cases} \quad (83)$$



The integral

$$\begin{aligned} & \left( \begin{array}{c} n_1 l_1 m_1 n_2 l_2 m_2 \\ r_{12} \end{array} \left| \begin{array}{c} n'_1 l'_1 m'_1 n'_2 l'_2 m'_2 \end{array} \right. \right) \\ &= \iint \varphi^*(n_1 l_1 m_1 | \mathbf{r}_1) \varphi^*(n_2 l_2 m_2 | \mathbf{r}_2) \frac{1}{r_{12}} \varphi(n'_1 l'_1 m'_1 | \mathbf{r}_1) \varphi(n'_2 l'_2 m'_2 | \mathbf{r}_2) d\tau \end{aligned}$$

is therefore given by

$$\begin{aligned} & \left( \begin{array}{c} n_1 l_1 m_1 n_2 l_2 m_2 \\ r_{12} \end{array} \left| \begin{array}{c} n'_1 l'_1 m'_1 n'_2 l'_2 m'_2 \end{array} \right. \right) \\ &= \sum_{\lambda} (l_1 m_1 l_2 m_2 | P_{\lambda}(\cos \omega) | l'_1 m'_1 l'_2 m'_2) R_{\lambda}(n_1 l_1 n_2 l_2 n'_1 l'_1 n'_2 l'_2) \end{aligned} \quad (84)$$

where

$$\begin{aligned} & (l_1 m_1 l_2 m_2 | P_{\lambda}(\cos \omega) | l'_1 m'_1 l'_2 m'_2) \\ &= \iint Y_{l_1 m_1}^*(\hat{\mathbf{r}}_1) Y_{l_2 m_2}^*(\hat{\mathbf{r}}_2) P_{\lambda}(\cos \omega) Y_{l'_1 m'_1}(\hat{\mathbf{r}}_1) Y_{l'_2 m'_2}(\hat{\mathbf{r}}_2) d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2 \end{aligned} \quad (85)$$

$$R_{\lambda}(abcd) = \iint P_a(r_1) P_b(r_2) \gamma_{\lambda}(r_1, r_2) P_c(r_1) P_d(r_2) dr_1 dr_2 \quad (86)$$

It may be mentioned straight away that the sum over  $\lambda$  in (84) in practice rarely contains more than two or three nonzero terms; for  $lsnl$  states it is in fact only one nonzero term.

From the definition (83) of  $\gamma_{\lambda}(r_1, r_2)$  the integral  $R_{\lambda}$  may be written

$$R_{\lambda}(abcd) = \int_0^{\infty} P_a(r_1) P_c(r_1) \gamma_{\lambda}(P_b P_d | r_1) dr_1 \quad (87)$$

where

$$\gamma_{\lambda}(P_a P_c | r_1) = \frac{1}{r_1^{\lambda+1}} \int_0^{r_1} P_b(r_2) P_d(r_2) r_2^{\lambda} dr_2 + r_1^{\lambda} \int_{r_1}^{\infty} P_b(r_2) P_d(r_2) \frac{1}{r_2^{\lambda+1}} dr_2 \quad (88)$$

An alternative expression for  $R_{\lambda}$  is obvious

$$R_{\lambda}(abcd) = \int_0^{\infty} P_b(r_2) P_d(r_2) \gamma_{\lambda}(P_a P_c | r_2) dr_2$$

From the direct integrals we obtain radial integrals of the type  $R_\lambda(abab)$  and from the exchange integrals we obtain  $R_\lambda(abba)$ . For these it is usual to introduce the special symbols

$$F_\lambda(ab) = R_\lambda(abab), \quad G_\lambda(ab) = R_\lambda(abba). \quad (89)$$

In order to evaluate the angular integrals (85) we require the spherical harmonic addition theorem,<sup>3,8,9,13</sup>

$$P_\lambda(\cos \omega) = \sum C_{\lambda\mu}^*(\hat{\mathbf{r}}_1) C_{\lambda\mu}(\hat{\mathbf{r}}_2) \quad (90)$$

with<sup>4</sup>

$$C_{\lambda\mu}(\hat{\mathbf{r}}) = \left( \frac{4\pi}{2\lambda+1} \right)^{1/2} Y_{\lambda\mu}(\hat{\mathbf{r}}) \quad (91)$$

From (85) and (90) we obtain

$$(l_1 m_1 l_2 m_2 | P_\lambda | l'_1 m'_1 l'_2 m'_2) = \sum_{\mu} (l_1 m_1 | C_{\lambda\mu}^* | l'_1 m'_1) (l_2 m_2 | C_{\lambda\mu} | l'_2 m'_2) \quad (92)$$

with

$$(lm | C_{\lambda\mu} | l'm') = \int Y_{lm}^*(\hat{\mathbf{r}}) C_{\lambda\mu}(\hat{\mathbf{r}}) Y_{l'm'}(\hat{\mathbf{r}}) d\hat{\mathbf{r}}. \quad (93)$$

Since  $(lm | C_{\lambda\mu} | l'm')$  involves an integral

$$\int_0^{2\pi} \exp [i(-m + \mu + m')\varphi] d\varphi$$

it will vanish unless  $\mu = m - m'$ . Condon and Shortley<sup>3</sup> (p. 178) tabulate  $c^\lambda(lm, l'm') = (lm | C_{\lambda m - m'} | l'm')$ . Racah<sup>7</sup> obtains the expression

$$(lm | C_{\lambda\mu} | l'm') = \left[ \frac{(2l' + 1)}{(2l + 1)} \right]^{1/2} (l' \lambda 0 0 | l' \lambda 0) (l' \lambda m' \mu | l' \lambda m)$$

in terms of the vector coupling coefficients defined in § 7.3

\* Spherical harmonics with normalization (91) are used by Racah.<sup>7</sup> This form is usually the most convenient when the spherical harmonics appear as operators rather than as eigenfunctions.

The integrals occurring for  $1snl$  configurations may be evaluated using only the spherical harmonic orthonormality relation (22). One obtains

$$(00|C_{\lambda\mu}|00) = \delta_{\lambda 0}\delta_{\mu 0}$$

$$(lm|C_{00}|lm) = 1$$

$$(00|C_{\lambda\mu}|lm) = \frac{1}{(2l+1)^{1/2}} \delta_{\lambda l} \delta_{\mu, -m}$$

and hence

$$(00lm|P_{\lambda}|00lm) = \delta_{\lambda 0}$$

$$(00lm|P_{\lambda}|lm00) = \frac{\delta_{\lambda l}}{(2l+1)}$$

The complete electrostatic energy for  $1snl$  configurations is therefore

$$E(1snl) = I(1s) + I(nl) + F_0(1snl) \pm \frac{1}{(2l+1)} G_1(1snl). \quad (94)$$

### 9.6 Calculation of $E(1s2p)$

In the region where the  $1s$  function is large we may expect the potential to be dominated by the nuclear potential. Neglecting screening of the nucleus by the  $2p$  electron we take the  $1s$  radial function to be a  $\text{He}^+$  function, that is

$$P_{1s}(r) = 2^{-1/2} r e^{-2r}$$

The  $2p$  function will be large at much greater radial distances and we expect the nucleus to be effectively screened by the  $1s$  function (this may be justified by the fact that the effective charge  $Z_{2p}$  is not far different from unity). For  $2p$  we therefore use a hydrogen radial function

$$P_{2p}(r) = (1/2\sqrt{6}) r^2 e^{-r/2}.$$

Substitution of these functions in (94) gives results shown in Table IV.

TABLE IV  
ENERGY IN ATOMIC UNITS (27.20 ev)

	Calculated		Observed	
He $1s2p\ ^1P$	-2.1222		-2.1238	
He $1s2p\ ^3P$	-2.1299	-0.0077	-2.1332	-0.0094

The energy of  $\text{He}^+$  is  $-2$  atomic units. The calculated energy needed to remove a  $2p$  electron from  $\text{He } 1s2p^1P$  is therefore 0.1222 atomic units which may be compared with the energy of 0.125 atomic units required to remove a  $2p$  electron from hydrogen. The calculation therefore agrees with observation in giving a term value for  $\text{He } 1s2p^1P$  which is less than that for  $\text{H } 2p$ . Had we neglected exchange terms in the calculation we would have obtained 0.1260 atomic units for the detachment energy which would have been greater than that for  $\text{H } 2p$ .

The calculated singlet-triplet separations are seen to agree reasonably well with experiment.

## 10. Closed Shells and One Electron Outside of Closed Shells

We shall consider complex atom wave functions which may be built up from one-electron orbitals  $\varphi(\alpha_i|\mathbf{x}_i)$ . The expressions for the total energy will contain integrals of three types. Firstly there will be integrals  $I(\alpha_i)$  for the kinetic energy, together with the potential energy in the field of the nucleus, of the electron with quantum numbers  $\alpha_i$ . Secondly there will be integrals  $(\alpha_i\alpha_j|1/r_{12}|\alpha_i\alpha_j)$  for the electrostatic interaction energy between electron pairs. And thirdly there will be exchange integrals  $(\alpha_i\alpha_j|1/r_{12}|\alpha_j\alpha_i)$ .

In the present section we consider the energies of closed shells and the interaction of an outer electron with closed shells.

### 10.1 States Which May Be Represented in Terms of Single $D$ Functions

In § 5.2. we introduced the antisymmetric functions  $D(A|\mathbf{X})$  where  $\mathbf{X}$  stands for the coordinates  $(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$  and where  $A$  might specify the quantum numbers

$$A = (n_1 l_1 m_{1i} m_{1s}, n_2 l_2 m_{2i} m_{2s}, \dots, n_N l_N m_{Ni} m_{Ns}).$$

For a closed shell  $\Sigma_i m_{i\alpha} = \Sigma_i m_{is} = 0$  and therefore  $S = L = 0$ . A closed shell may be represented by\* a single  $D$  function, that for which  $N = 4l + 2$ ,  $n_1 l_1 = n_2 l_2 = \dots = nl$ , and in which the quantum numbers  $m_{i\alpha}, m_{is}$  take on all allowed values.

For configurations  $nl^{4l+2}n'l'$  containing one electron outside of closed shells one has  $S = s = \frac{1}{2}$ ,  $L = l'$ ,  $M_S = m'_s$  and  $M_L = m'_l$ . It may be seen that a single  $D$  function may also be used for configurations of this type.

\* In general it is necessary to employ linear combinations of  $D$ -functions in order to diagonalize the energy matrix within a configuration.

It may be shown in a similar way that single  $D$  functions may also be used for configurations  $n^{4l+1}$  in which the number of electrons is one less than the number required to complete a closed shell.

We first consider properties of states which may be represented by single  $D$  functions.

## 10.2 The Normalization of $D$ Functions

From the definition of a determinant it follows that a  $D$  function defined by (41) is equal to

$$D(A|\mathbf{X}) = \frac{1}{\sqrt{N!}} \sum (-1)^p \varphi(\alpha_q|\mathbf{x}_1) \varphi(\alpha_s|\mathbf{x}_2) \varphi(\alpha_t|\mathbf{x}_3) \dots \quad (95)$$

where  $(q, s, t, \dots)$  is a permutation of the numbers  $(1, 2, 3, \dots)$ ,  $p$  is the parity of the permutation\* and the sum is over all such permutations. Assuming that

$$(\alpha_i|\alpha_j) = \delta_{ij} \quad (96)$$

(see § 5.2) we show that  $D$  will be normalized to unity. Using (95) we have

$$(A|A) = \int D^*(A|\mathbf{X}) D(A|\mathbf{X}) d\mathbf{X} = \frac{1}{N!} \sum_{PP'} (-1)^{p+p'} (\alpha_q|\alpha_{q'}) (\alpha_s|\alpha_{s'}) (\alpha_t|\alpha_{t'}) \dots \quad (97)$$

where  $(q', s', t', \dots)$  is a permutation with parity  $p'$ . By (96) the summand of (97) is zero for  $(q, s, t, \dots) \neq (q', s', t', \dots)$  and unity for  $(q, s, t, \dots) = (q', s', t', \dots)$ . The number of permutations  $P$  is  $N!$  and therefore  $(A|A) = 1$ .

## 10.3 Energies of States Represented by Single $D$ Functions

We consider the evaluation of

$$(A|H|A) = \int D^*(A|\mathbf{X}) H D(A|\mathbf{X}) d\mathbf{X}$$

with

$$H = \sum_{i=1}^N H_1(\mathbf{x}_i) + \sum_{i,j=1}^N \frac{1}{r_{ij}}$$

\* The numbers  $(q, s, t, \dots)$  may be permuted to the numbers  $(1, 2, 3, \dots)$  by successive interchanges of pairs of numbers. With given  $(q, s, t, \dots)$  the number of interchanges is uniquely even or odd,  $p$  is even or odd according to whether the number of interchanges is even or odd.

Since  $D^*D$  is a symmetric function of the coordinates we have

$$\sum_{i=1}^N H_1(\mathbf{x}_i) \left| A \right\rangle = N(A | H_1(\mathbf{x}_1) | A)$$

and using the expansion (95),

$$\left( A \left| \sum H_1(\mathbf{x}_i) \right| A \right) = \frac{1}{(N-1)!} \sum_{PP'} (-1)^{p+p'} (\alpha_q | H_1 | \alpha_{q'}) (\alpha_s | \alpha_{s'}) (\alpha_t | \alpha_{t'}) \dots$$

The summand vanishes unless  $(s, t, \dots) = (s', t', \dots)$  and therefore

$$\sum' H_1(\mathbf{x}_i) \left| A \right\rangle = \frac{1}{(N-1)!} \sum_n (\alpha_q | H_1 | \alpha_q) (\alpha_s | \alpha_s) (\alpha_t | \alpha_t) \dots$$

Since  $(\alpha_s | \alpha_s) (\alpha_t | \alpha_t) \dots = 1$  and since there are  $(N-1)!$  permutations of the  $(N-1)$  numbers  $(s, t, \dots)$  we obtain

$$\sum_{i=1}^N H_1(\mathbf{x}_i) \left| A \right\rangle = \sum_{q=1}^N (\alpha_q | H_1 | \alpha_q) \quad (98)$$

In the sum†  $\sum' 1/r_{ij}$ , there are  $\frac{1}{2}N(N-1)$  terms. Using again the fact that  $D^*D$  is symmetric we obtain

$$\left( A \left| \sum'_{i,j} \frac{1}{r_{ij}} \right| A \right) = \frac{1}{2} N(N-1) \left( A \left| \frac{1}{r_{12}} \right| A \right)$$

and, by (95),

$$\left( A \left| \sum'_{i,j} \frac{1}{r_{ij}} \right| A \right) = \frac{1}{2(N-2)!} \sum_{PP'} (-1)^{p+p'} \begin{pmatrix} \alpha_q \alpha_s & 1 & \alpha_{q'} \alpha_{s'} \\ & r_{12} & \end{pmatrix} \times \quad (99)$$

$$(\alpha_t | \alpha_{t'}) (\alpha_u | \alpha_{u'}) \dots$$

where

$$\begin{pmatrix} \alpha_q \alpha_s & 1 & \alpha_{q'} \alpha_{s'} \\ & r_{12} & \end{pmatrix} = \iint \varphi^*(\alpha_q | \mathbf{x}_1) \varphi^*(\alpha_s | \mathbf{x}_2) \frac{1}{r_{12}} \varphi(\alpha_{q'} | \mathbf{x}_1) \varphi(\alpha_{s'} | \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2.$$

In (99) the summand vanishes unless  $(q', s', t', u', \dots)$  is equal to  $(q, s, t, u, \dots)$  or to  $(s, q, t, u, \dots)$ . In the first case  $(-1)^{p+p'} = +1$  and in the second  $(-1)^{p+p'} = -1$ . Therefore

† It will be recalled that the sum  $\sum'$  is over all pairs  $i, j$ , excluding  $i = j$ , each pair being counted once only.

$$\sum' \frac{1}{r_{12}} A = \frac{1}{2(N-2)!} \sum_n \left[ \left( \alpha_q \alpha_s \left| \frac{1}{r_{12}} \right| \alpha_q \alpha_s \right) - \left( \alpha_q \alpha_s \left| \frac{1}{r_{12}} \right| \alpha_s \alpha_q \right) \right] \times (\alpha_t | \alpha_t) (\alpha_u | \alpha_u) \dots$$

Since there are  $(N-2)!$  permutations of the  $(N-2)$  numbers  $(t, u, \dots)$  we obtain

$$\sum' \frac{1}{r_{12}} A = \frac{1}{2} \sum_{q,s} \left( \alpha_q \alpha_s \left| \frac{1}{r_{12}} \right| \alpha_q \alpha_s \right) - \left( \alpha_q \alpha_s \left| \frac{1}{r_{12}} \right| \alpha_s \alpha_q \right)$$

the sum being over all values of  $q, s$ , with  $q \neq s$ . In terms of the sum in which each pair is counted once only we have

$$\sum' \frac{1}{r_{12}} A = \sum_{i,j} \left[ \left( \alpha_q \alpha_s \left| \frac{1}{r_{12}} \right| \alpha_q \alpha_s \right) - \left( \alpha_q \alpha_s \left| \frac{1}{r_{12}} \right| \alpha_s \alpha_q \right) \right] \quad (100)$$

In this expression one may, if convenient, include  $q = s$  in the summation since, for  $q = s$ , the direct matrix element  $(\alpha_q \alpha_s | 1/r_{12} | \alpha_q \alpha_s)$  is equal to the exchange matrix element  $(\alpha_q \alpha_s | 1/r_{12} | \alpha_s \alpha_q)$ .

#### 10.4 Interaction Between an Electron and a Closed Shell

The interaction energy between an electron  $n'l'm'_i m'_s$  and the closed shell  $nl^{4l+2}$  is

$$\sum_{n_l m_s} \left[ \left( n l m_i m_s n' l' m'_i m'_s \left| \frac{1}{r_{12}} \right| n l m_i m_s n' l' m'_i m'_s \right) - \left( n l m_i m_s n' l' m'_i m'_s \left| \frac{1}{r_{12}} \right| n' l' m'_i m'_s n l m_i m_s \right) \right] \quad (101)$$

this expression being obtained from (100). The sum over  $m_s$  gives a factor 2 in the expression for the direct matrix element while the exchange matrix element is zero unless  $m_s = m'_s$ . The expression (101) is therefore equal to

$$\sum \left[ 2 \left( n l m_i n' l' m'_i \left| \frac{1}{r_{12}} \right| n l m_i n' l' m'_i \right) - \left( n l m_i n' l' m'_i \left| \frac{1}{r_{12}} \right| n' l' m'_i n l m_i \right) \right]$$

Using the expansion (83) for  $(1/r_{12})$  this may now be written

$$\sum [f_\lambda(l^{4l+2}l') F_\lambda(nl n'l') - g_\lambda(l^{4l+2}l') G_\lambda(nl n'l')] \quad (102)$$

where

$$f_{\lambda}(l^{4l}+2l') = 2 \sum_{m_l} (lm_l l' m'_l | P_{\lambda}(\cos \omega) | lm_l l' m'_l)$$

and

$$g_{\lambda}(l^{4l}+2l') = \sum_{m_l} (lm_l l' m'_l | P_{\lambda}(\cos \omega) | l' m'_l lm_l),$$

the  $P_{\lambda}$  matrix elements being defined by (85) and  $F_{\lambda}, G_{\lambda}$  being defined by (86) and (89).

To evaluate the coefficients we may use the fact that  $f_{\lambda}$  and  $g_{\lambda}$  do not depend on  $m'_l$  (§ 7.8.); the expressions for  $f_{\lambda}$  and  $g_{\lambda}$  may therefore be summed over  $m'_l$  and divided by  $(2l' + 1)$ . Putting  $\hat{\mathbf{r}}_1 = \hat{\mathbf{r}}_2$  in the spherical harmonic addition theorem (90) and using the fact that  $P_l(1) = 1$  we have

$$\sum_{m_l} Y_{lm_l}^*(\hat{\mathbf{r}}_1) Y_{lm_l}(\hat{\mathbf{r}}_1) = \frac{(2l+1)}{4\pi}.$$

This tells us that a closed shell has a spherically symmetric charge distribution. The expression for  $f_{\lambda}$  therefore becomes

$$f_{\lambda} = \frac{2(2l+1)}{(4\pi)^2} \iint P_{\lambda}(\cos \omega) d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2.$$

Since the integrand now depends only on  $\cos \omega$  we may replace  $d\hat{\mathbf{r}}_1$  by  $2\pi \sin \omega d\omega$  and carry out the integration over  $d\hat{\mathbf{r}}_2$  to obtain a factor of  $4\pi$ . Since

$$\int_0^{\pi} P_{\lambda}(\cos \omega) 2\pi \sin \omega d\omega = 4\pi \delta_{\lambda 0}$$

we obtain

$$f_{\lambda}(l^{4l}+2l') = 2(2l+1) \delta_{\lambda 0}. \quad (103)$$

Using the addition theorem (90) in the form

$$\sum_{m''} Y_{l'm''}^*(\hat{\mathbf{r}}_1) Y_{l''m''}(\hat{\mathbf{r}}_2) = \left( \frac{2l''+1}{4\pi} \right) P_{l''}(\cos \omega)$$

we obtain

$$g_{\lambda} = \frac{1}{(2l'+1)} \sum_{m_l m'_l} \iint Y_{lm_l}^*(\hat{\mathbf{r}}_1) Y_{l'm'_l}^*(\hat{\mathbf{r}}_2) P_{\lambda}(\cos \omega) Y_{l'm'_l}(\hat{\mathbf{r}}_1) Y_{lm_l}(\hat{\mathbf{r}}_2) d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2$$

$$= \frac{1}{(2l'+1)} \frac{(2l+1)}{4\pi} \frac{(2l'+1)}{4\pi} \iint P_l(\cos \omega) P_{\lambda}(\cos \omega) P_{l'}(\cos \omega) d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2.$$



# I COMPLEX ATOMS

Since the integrand again depends only on  $\cos \omega$  we have

$$g_{\lambda}(l^{4l+2}l') = \frac{1}{2} (2l + 1) C_{ll'} \quad (104)$$

where

$$C_{ll'} = \int_{-1}^{+1} P_l(t) P_{\lambda}(t) P_{l'}(t) dt \quad (105)$$

It is obvious that  $C_{ll'}$  is independent of the order of the numbers  $ll'$ . It may be shown that  $C_{ll'}$  is zero unless

$$\begin{aligned} |l - l'| &\leq \lambda \leq (l + l'), \\ (l + \lambda + l') &= \text{an even integer} \end{aligned} \quad (106)$$

Some values of  $C_{ll'}$  are given in Table V

TABLE V  
THE COEFFICIENT  $C_{ll'}$

$ll'$	$\lambda$	$C_{ll'}$
$ss$	0	2
$sp$	1	2/3
$sd$	2	2/5
$pp$	0	2/3
	2	4/15
$pd$	1	4/15
	3	6/35
$dd$	0	2/5
	2	4/35
	4	4/35

The final expression for the interaction energy between  $n l^{4l+2}$  and  $n' l'$  is

$$(2l + 1) \left[ 2F_0(n l n' l') - \frac{1}{2} \sum_{\lambda} C_{ll'} G_{\lambda}(n l n' l') \right]. \quad (107)$$

### 10.5 Interaction Between Two Closed Shells

The interaction energy

$$2(2l+1)(2l'+1) \left\{ 2F_0(nln'l') - \frac{1}{2} \sum_{\lambda} C_{ll'l'} G_{\lambda}(nln'l') \right\} \quad (108)$$

between  $nl^{4l+2}$  and  $n'l'^{4l'+2}$  is obtained on multiplying (107) by  $2(2l'+1)$ .

### 10.6 The Energy of a Closed Shell

The interaction energy

$$(2l+1)^2 \left\{ 2F_0(nlnl) - \frac{1}{2} \sum_{\lambda} C_{lll} F_{\lambda}(nlnl) \right\} \quad (109)$$

for the electrons in the closed shell  $nl^{4l+2}$  is obtained on putting  $(n'l') = (nl)$  in (108) and dividing by 2 since each pair of electrons must be counted once only. It should be noted that  $G_{\lambda}(nlnl) = F_{\lambda}(nlnl)$ . From (105) we have

$$C_{l0l} = \int_{-1}^{+1} P_l(t) P_l(t) dt = \frac{2}{(2l+1)}$$

and we may therefore write (109) as

$$\frac{1}{2} (4l+2)(4l+1) F_0(nlnl) - \frac{(2l+1)^2}{2} \sum_{\lambda \neq 0} C_{lll} F_{\lambda}(nlnl). \quad (110)$$

The coefficient  $\frac{1}{2}(4l+2)(4l+1)$  of  $F_0$  is equal to the number of pairs which can be obtained with  $(4l+2)$  electrons.

### 10.7 Energy Expressions for $\text{Na}^+$ and Na

As examples of the formulas obtained we consider the expressions for the energies of  $\text{Na}^+$  and Na in terms of radial integrals. For the  $1s^2 2s^2 2p^6$  configuration of  $\text{Na}^+$  one obtains

$$\begin{aligned} E(1s^2 2s^2 2p^6) = & 2I(1s) + 2I(2s) + 6I(2p) + \\ & F_0(1s1s) + 12F_0(1s2p) - 2G_1(1s2p) + \\ & F_0(2s2s) + 12F_0(2s2p) - 2G_1(2s2p) + \\ & 4F_0(1s2s) - G_0(1s2s) + \\ & 15F_0(2p2p) - \frac{6}{5} F_2(2p2p). \end{aligned} \quad (111)$$

For the  $1s^2 2s^2 2p^6 nl$  configuration of neutral Na one usually neglects perturbations of the  $1s^2 2s^2 2p^6 \text{Na}^+$  core by the  $nl$  valence electron. Let  $E(nl)$  be the energy required to remove the valence electron. This is equal to  $I(nl)$  plus the interaction energy between  $nl$  and the  $\text{Na}^+$  core. One obtains

$$\begin{aligned}
 E(nl) = I(nl) + 2F_0(1snl) - \frac{1}{(2l+1)} G_1(1snl) + \\
 2F_0(2snl) - \frac{1}{(2l+1)} G_1(2snl) + \\
 6F_0(2pnl) - \frac{3}{2} \sum_{\lambda} C_{1\lambda} G_{\lambda}(2pnl).
 \end{aligned} \tag{112}$$

## 11. Two Electrons Outside of Closed Shells

### 11.1 Allowed Values of $SL$

With two electrons  $n_1 l_1, n_2 l_2$  outside of closed shells the values of  $S$  and  $L$  for the whole system are obtained on coupling the angular momenta of the electrons  $n_1 l_1, n_2 l_2$ . For two inequivalent electrons ( $n_1 l_1 \neq n_2 l_2$ ) the exclusion principle imposes no restrictions on  $m_{s_1} m_{l_1}, m_{s_2} m_{l_2}$  and we can have  $S = 0$  or  $1$ , and  $L = (l_1 + l_2), (l_1 + l_2 - 1), \dots, |l_1 - l_2|$ . For two equivalent electrons ( $n_1 l_1 = n_2 l_2$ ) the exclusion principle imposes the restriction  $m_{s_1} m_{l_1} \neq m_{s_2} m_{l_2}$ ; this will be seen to imply certain restrictions on the allowed values of  $SL$ .

### 11.2 Interactions With Closed Shells

The interaction energy between a closed shell and an electron  $n'l'$  does not depend on  $m'_s m'_l$ . It follows that the expression for the interaction energy between  $n_1 l_1, n_2 l_2$  and closed shells will not depend on\*  $SL$ ; thus for states  $n l'^{4l+2} n_1 l_1 n_2 l_2 SL$  the interaction energy between  $n_1 l_1$  and  $n l'^{4l+2}$  is obtained from (107) on replacing  $n'l'$  by  $n_1 l_1$ . In discussing energy differences between  $n_1 l_1 n_2 l_2 SL$  states the closed shells will be neglected.

\* The interaction energy itself may depend on  $SL$  if different radial functions  $P_{n_1 l_1}, P_{n_2 l_2}$  are used for different values of  $SL$ .

### 11.3 Two-Electron Wave Functions

As in § 9.1. an antisymmetric two-electron wave function may be written as the product of a spin function and a function of  $\mathbf{r}_1, \mathbf{r}_2$ ;

$$\Psi(n_1 l_1 n_2 l_2 S L M_S M_L | \mathbf{x}_1, \mathbf{x}_2) = \psi(S M_S | \sigma_1, \sigma_2) \psi_{\pm}(n_1 l_1 n_2 l_2 L M_L | \mathbf{r}_1, \mathbf{r}_2). \quad (113)$$

The symmetric function  $\psi_+(\mathbf{r}_1, \mathbf{r}_2)$  goes with the singlet spin state, and the antisymmetric function  $\psi_-(\mathbf{r}_1, \mathbf{r}_2)$  with the triplet spin state. For two inequivalent electrons we have

$$\psi_{\pm}(n_1 l_1 n_2 l_2 L M_L | \mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \{ \psi(n_1 l_1 n_2 l_2 L M_L | \mathbf{r}_1, \mathbf{r}_2) \pm \psi(n_1 l_1 n_2 l_2 L M_L | \mathbf{r}_2, \mathbf{r}_1) \} \quad (114)$$

with

$$\psi(n_1 l_1 n_2 l_2 L M_L | \mathbf{r}_1, \mathbf{r}_2) = \frac{1}{r_1} P_{n_1 l_1}(r_1) \frac{1}{r_2} P_{n_2 l_2}(r_2) \times \psi(l_1 l_2 L M_L | \hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \quad (115)$$

and

$$\psi(l_1 l_2 L M_L | \hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = \sum_{m_1 m_2} (l_1 l_2 m_1 m_2 | l_1 l_2 L M_L) Y_{l_1 m_1}(\hat{\mathbf{r}}_1) Y_{l_2 m_2}(\hat{\mathbf{r}}_2). \quad (116)$$

The function  $\Psi$  is then readily shown to be normalized to unity if

$$\int P_{n_1 l_1}^2 dr = \int P_{n_2 l_2}^2 dr = 1, \quad \int P_{n_1 l_1} P_{n_2 l_2} dr = 0. \quad (117)$$

For two equivalent electrons ( $n_1 l_1 = n_2 l_2 = n l$ ) the function  $\psi(n l n l L M_L | \mathbf{r}_1, \mathbf{r}_2)$  is symmetric for even  $L$  and antisymmetric for odd  $L$  (§ 7.7). The function

$$\Psi(n l^2 S L M_S M_L | \mathbf{x}_1, \mathbf{x}_2) = \psi(S M_S | \sigma_1, \sigma_2) \psi(n l n l L M_L | \mathbf{r}_1, \mathbf{r}_2) \quad (118)$$

is therefore automatically antisymmetric for  $(S + L)$  even, and symmetric for  $(S + L)$  odd. This function, formed by direct use of the vector coupling formulas, will be normalized if  $P_{n l}$  is normalized. We conclude that, for two equivalent electrons, only even values of  $(S + L)$  are allowed by the exclusion principle. Thus for the  $2p^2$  configuration the allowed values\* of  $(SL)$  are  $^1S, ^1D$  and  $^3P$ . For a configuration such as  $2p^3 3p$  containing two inequivalent  $p$  electrons the allowed values of  $(SL)$  would be  $^1S, ^1P, ^1D, ^3S, ^3P$  and  $^3D$ .

\* For an alternative derivation<sup>5, 6</sup> one could list the values of  $m_s, m_{l_1}, m_s, m_{l_2}$  allowed by the exclusion principle and deduce the allowed values of  $SL$  by an obvious generalization of the argument leading to (63).

## 11.4 The Electrostatic Energies: Theory

For two inequivalent electrons the wave function may be written†

$$\Psi(n_1 l_1 n_2 l_2 SL | \mathbf{x}_1, \mathbf{x}_2) = \psi(S | \sigma_1, \sigma_2) \frac{1}{\sqrt{2}} \cdot \quad (119)$$

$$\{\psi(n_1 l_1 n_2 l_2 L | \mathbf{r}_1, \mathbf{r}_2) + (-1)^S \psi(n_1 l_1 n_2 l_2 L | \mathbf{r}_2, \mathbf{r}_1)\}.$$

The radial functions will be assumed to satisfy (117). We consider the evaluation of

$$E(n_1 l_1 n_2 l_2 SL) = (n_1 l_1 n_2 l_2 SL | H | n_1 l_1 n_2 l_2 SL)$$

with

$$H = H_1(\mathbf{r}_1) + H_2(\mathbf{r}_2) + \frac{1}{r_{12}}$$

Since  $H$  is symmetric one obtains

$$E = \int \psi^*(n_1 l_1 n_2 l_2 L | \mathbf{r}_1, \mathbf{r}_2) H \psi(n_1 l_1 n_2 l_2 L | \mathbf{r}_1, \mathbf{r}_2) d\tau +$$

$$(-1)^S \int \psi^*(n_1 l_1 n_2 l_2 L | \mathbf{r}_1, \mathbf{r}_2) H \psi(n_1 l_1 n_2 l_2 L | \mathbf{r}_2, \mathbf{r}_1) d\tau$$

(see § 9.3.). Using the orthonormality relations (66) for the vector coupling coefficients one obtains for the direct matrix element of  $H_1(\mathbf{r}_1)$

$$\int \psi^*(n_1 l_1 n_2 l_2 L | \mathbf{r}_1, \mathbf{r}_2) H_1(\mathbf{r}_1) \psi(n_1 l_1 n_2 l_2 L | \mathbf{r}_1, \mathbf{r}_2) d\tau = I(n_1 l_1)$$

where  $I(n_1 l_1)$  is defined by (74). Similarly, the direct matrix element of  $H_1(\mathbf{r}_2)$  is  $I(n_2 l_2)$ . That the exchange matrix elements of  $H_1(\mathbf{r}_1)$  and  $H_1(\mathbf{r}_2)$  are zero follows from the orthogonality of the radial functions. It remains to evaluate the matrix elements of  $1/r_{12}$ . Using (115) and the expansion (83) for  $1/r_{12}$  one obtains

$$\int \psi^*(n_1 l_1 n_2 l_2 L | \mathbf{r}_1, \mathbf{r}_2) \frac{1}{r_{12}} \psi(n_1 l_1 n_2 l_2 L | \mathbf{r}_1, \mathbf{r}_2) d\tau = \sum_{\lambda} f_{\lambda}(l_1 l_2 L) F_{\lambda}(n_1 l_1 n_2 l_2) \quad (120)$$

and

$$\int \psi^*(n_1 l_1 n_2 l_2 L | \mathbf{r}_1, \mathbf{r}_2) \frac{1}{r_{12}} \psi(n_1 l_1 n_2 l_2 L | \mathbf{r}_2, \mathbf{r}_1) d\tau = \sum_{\lambda} g_{\lambda}(l_1 l_2 L) G_{\lambda}(n_1 l_1 n_2 l_2) \quad (121)$$

† Specification of the quantum numbers  $M_S M_L$  is omitted when inessential.

where  $F_\lambda$  and  $G_\lambda$  are defined by (89) and where

$$f_\lambda(l_1 l_2 L) = \int \psi^*(l_1 l_2 L | \hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) P_\lambda(\cos \omega) \psi(l_1 l_2 L | \hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2 \quad (122)$$

and

$$g_\lambda(l_1 l_2 L) = \int \psi^*(l_1 l_2 L | \hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) P_\lambda(\cos \omega) \psi(l_1 \check{l}_2 L | \hat{\mathbf{r}}_2, \hat{\mathbf{r}}_1) d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2. \quad (123)$$

The complete energy expression is therefore

$$E(n_1 l_1 n_2 l_2 SL) = I(n_1 l_1) + I(n_2 l_2) + \quad (124)$$

$$\sum_{\lambda} [f_\lambda(l_1 l_2 L) F_\lambda(n_1 l_1 n_2 l_2) + (-1)^S g_\lambda(l_1 l_2 L) G_\lambda(n_1 l_1 n_2 l_2)].$$

Closed algebraic expressions for the coefficients  $f_\lambda(l_1 l_2 L)$  and  $g_\lambda(l_1 l_2 L)$  may be obtained using tensor operator methods<sup>7-9</sup>. Some numerical values are given in Table VI. It may be noted that

$$\begin{aligned} f_\lambda(l_1 l_2 L) &= f_\lambda(l_2 l_1 L), & g_\lambda(l_1 l_2 L) &= g_\lambda(l_2 l_1 L), \\ f_0(l_1 l_2 L) &= 1, & g_0(l_1 l_2 L) &= (-1)^L \delta_{l_1 l_2}. \end{aligned} \quad (125)$$

TABLE VI  
THE COEFFICIENTS  $f_\lambda$  AND  $g_\lambda$

$l_1 l_2$	$L$	$f_0$	$f_2$	$f_4$	$g_0$	$g_1$	$g_2$	$g_3$	$g_4$
<i>ss</i>	<i>S</i>	+1	—	—	+1	—	—	—	—
<i>sp</i>	<i>P</i>	+1	—	—	—	+1/3	—	—	—
<i>sd</i>	<i>D</i>	+1	—	—	—	—	+1/5	—	—
<i>pp</i>	<i>S</i>	+1	+10/25	—	+1	—	+10/25	—	—
	<i>P</i>	+1	—5/25	—	—1	—	+5/25	—	—
	<i>D</i>	+1	+1/25	—	+1	—	+1/25	—	—
<i>pd</i>	<i>P</i>	+1	+7/35	—	—	+1/15	—	+63/245	—
	<i>D</i>	+1	—7/35	—	—	—3/15	—	+21/245	—
	<i>F</i>	+1	+2/35	—	—	+6/15	—	+3/245	—
<i>dd</i>	<i>S</i>	+1	+14/49	+126/441	+1	—	+14/49	—	+126/441
	<i>P</i>	+1	+7/49	—84/441	—1	—	—7/49	—	+86/441
	<i>D</i>	+1	—3/49	+36/441	+1	—	—3/49	—	+36/441
	<i>F</i>	+1	—8/49	—9/441	—1	—	+8/49	—	+9/441
	<i>G</i>	+1	+4/49	+1/441	+1	—	+4/49	—	+1/441

In practice one rarely obtains more than two or three nonzero terms in the sum over  $\lambda$ .

Using (118) for two equivalent electrons one obtains

$$E(nl^2SL) = 2I(nl) + \sum f_{\lambda}(llL)F_{\lambda}(nl nl) \quad ((S+L) \text{ even}). \quad (126)$$

### 11.5 The Electrostatic Energies: Comparison with Experiment

The general pattern of predicted energy levels may be compared with experimental results without making detailed calculations of the wave functions. We consider the levels of carbon, for which the ground configuration is  $1s^2 2s^2 2p^2$ .

For the ground configuration we expect to obtain the terms  $^3P$ ,  $^1D$  and  $^1S$ . The energy expressions are

$$SL \quad E(2p^2SL)$$

$$^1S \quad E_0 + \frac{10}{25} F_2$$

$$^1D \quad E_0 + \frac{1}{25} F_2$$

$$^3P \quad E_0 - \frac{5}{25} F_2$$

where  $E_0$  is the part of the energy which does not depend on  $SL$  and where  $F_2 = F_2(2p^2 2p)$  is positive. The three lowest energy levels of C may be identified\* with the predicted levels and occur in the predicted order.

Assuming that the same radial function may be used for each of the three terms we obtain for the predicted ratio of the separations

$$\frac{E(2p^2 ^1D) - E(2p^2 ^1S)}{E(2p^2 ^3P) - E(2p^2 ^1D)} = 1.5.$$

The observed ratio is 1.13. Improved agreement should be possible with more complicated wave functions.

For the  $2pns$  levels of C we obtain

$$E(2pns^{2S+1}P) = E_0 + (-1)^S G_1(2pns). \quad (127)$$

\* Complete identifications depend on consideration of fine structure, the Zeeman effect, and selection rules.

The  $^3P$  terms should therefore be lower than the singlets. This agrees with observation provided that  $n$  is not too large. The position for large  $n$  will be discussed in § 11.8.

For  $2pnp$  with  $n \neq 2$  the theory predicts six terms with energies.

$$\begin{array}{ll}
 L & E(2pnp^{2S+1}L) \\
 0 & E_0 + 0.40F_2 + (-1)^S[+G_0 + 0.40G_2] \\
 1 & E_0 - 0.20F_2 + (-1)^S[-G_0 + 0.20G_2] \\
 2 & E_0 + 0.04F_2 + (-1)^S[+G_0 + 0.04G_2]
 \end{array}$$

Thus for each  $2pnp$  configuration we have 6 observed energy levels and 4 unknown parameters 3 of which  $F_2(2pnp)$ ,  $G_0(2pnp)$ , and  $G_2(2pnp)$  should be positive. Determining the parameters for C  $2p3p$  by making a least squares fit, we obtain  $F_2 = 3706$ ,  $G_0 = 1393$ , and  $G_2 = 586$ , all in  $\text{cm}^{-1}$ . The energies calculated with these parameters are compared with observed energies in Table VII, the observed energies\* being reckoned from the lowest term,  $2p3p^1P$ . It is seen that reasonable agreement is obtained.

TABLE VII  
ENERGIES IN  $\text{cm}^{-1}$  FOR CARBON  $2p3p$

$SL$	(Obs.)	(Calc.)	(Calc.) - (Obs.)
$^1S$	5118	5169	+ 51
$^1D$	3753	3624	- 129
$^3P$	2517	2594	+ 77
$^3S$	1886	1915	+ 29
$^3D$	864	792	- 72
$^1P$	0	43	+ 43

## 11.6 The Spin-Orbit Energy in $LS$ Coupling: Theory

The spin-orbit Hamiltonian

$$H_{sp} = \xi(r_1)\mathbf{S}_1 \cdot \mathbf{L}_1 + \xi(r_2)\mathbf{S}_2 \cdot \mathbf{L}_2$$

commutes with  $\mathbf{J} = (\mathbf{S} + \mathbf{L})$  but does not commute with  $\mathbf{S}$  and  $\mathbf{L}$  separately. If the spin-orbit energy is small compared with the energy differences

\* We here consider the centres of gravity of the observed  $^3P$  and  $^3D$  terms; see § 11.5 below.



$E(n_1 l_1 n_2 l_2 SL) - E(n_1 l_1 n_2 l_2 S' L')$  between spectral terms one may neglect matrix elements

$$(n_1 l_1 n_2 l_2 SLJ | H_{sp} | n_1 l_1 n_2 l_2 S' L' J) \quad (128)$$

with  $(SL) \neq (S' L')$ . The spin-orbit energy is then given by

$$E_{sp}(n_1 l_1 n_2 l_2 SLJ) = (n_1 l_1 n_2 l_2 SLJ | H_{sp} | n_1 l_1 n_2 l_2 SLJ). \quad (129)$$

In the present section we consider the evaluation of this expression using a semiclassical argument: the same final result may be obtained using tensor operator methods

The problem is to calculate the mean value  $\overline{(\mathbf{S}_1 \cdot \mathbf{L}_1)}$  of  $\mathbf{S}_1 \cdot \mathbf{L}_1$  when spin-orbit energy is very small. When spin-orbit energy is zero  $\mathbf{L} = (\mathbf{L}_1 + \mathbf{L}_2)$  is a constant vector but, due to electrostatic coupling between the two electrons,  $\mathbf{L}_1$  and  $\mathbf{L}_2$  rotate around  $\mathbf{L}$ . As in the theory of the Zeeman effect (§ 3.6.) we therefore consider only the component of  $\mathbf{L}_1$  in the direction of  $\mathbf{L}$ . This component is  $\bar{\mathbf{L}}_1 = (\mathbf{L}_1 \cdot \mathbf{L})\mathbf{L}/L^2$ . In the same way we consider only the component  $\bar{\mathbf{S}}_1$  of  $\mathbf{S}_1$  in the direction of  $\mathbf{S}$ . Since  $\mathbf{S}_1 = \mathbf{S}_2$ ,  $\bar{\mathbf{S}}_1 = \frac{1}{2}\mathbf{S}$ . We then have

$$(\bar{\mathbf{S}}_1 \cdot \bar{\mathbf{L}}_1) = \frac{(\mathbf{L}_1 \cdot \mathbf{L})(\mathbf{S} \cdot \mathbf{L})}{2L^2}$$

We may now substitute  $(\mathbf{L}_1 \cdot \mathbf{L}) = \frac{1}{2}[L^2 + L_1^2 - L_2^2]$ ,  $(\mathbf{S} \cdot \mathbf{L}) = \frac{1}{2}[J^2 - S^2 - L^2]$  and make the usual correlations,  $L^2 \rightarrow L(L+1)\hbar^2$ ,  $L_1^2 \rightarrow l_1(l_1+1)\hbar^2$  etc. We obtain

$$(\mathbf{S}_1 \cdot \bar{\mathbf{L}}_1) = \hbar^2 \frac{[L(L+1) + l_1(l_1+1) - l_2(l_2+1)]}{4L(L+1)} \times \frac{1}{2} [J(J+1) - S(S+1) - L(L+1)]$$

The matrix element of  $H_{sp}$  is therefore

$$E_{sp}(n_1 l_1 n_2 l_2 SLJ) = \zeta(n_1 l_1 n_2 l_2 L) \cdot \frac{1}{2} [J(J+1) - S(S+1) - L(L+1)] \quad (130)$$

where

$$\zeta(n_1 l_1 n_2 l_2 L)$$

$$= \frac{[L(L+1) + l_1(l_1+1) - l_2(l_2+1)]\zeta(n_1 l_1) + [L(L+1) + l_2(l_2+1) - l_1(l_1+1)]\zeta(n_2 l_2)}{4L(L+1)}$$

and

$$\zeta(nl) = \hbar^2 \int_0^\infty P_{nl}(r) \xi(r) P_{nl}(r) dr. \quad (132)$$

From (130) we obtain the *Landé interval rule*,  $E(SLJ) - E(SLJ - 1) = \zeta J$ : the fine structure separation between adjacent levels is proportional to the larger  $J$  value. The  $LS$  coupling approximation will be valid when the fine structure separations satisfy the Landé rule and are small compared with the term separations  $E(SLJ) - E(S'L'J)$ .

The *centre of gravity* of a spectral term is defined by

$$\bar{E}(SL) = \frac{\sum_J (2J + 1) E(SLJ)}{(2L + 1)(2S + 1)}. \quad (133)$$

One may easily show that

$$\sum_{J=|S-L|}^{(S+L)} (2J + 1) [J(J + 1) - S(S + 1) - L(L + 1)] = 0.$$

In  $LS$  coupling the centre of gravity of a term is therefore equal to the term energy calculated neglecting spin-orbit interaction.

## 11.7 The Spin-Orbit Energy in $LS$ Coupling: Comparison with Experiment

To test the Landé rule we may use observed energies to calculate  $\zeta$  from

$$\zeta = [E(SLJ) - E(SLJ - 1)]/J.$$

This should not depend on  $J$ . Table VIII gives some results for  $nsnp\ ^3P_J$  levels. For Be the spin-orbit energy is not large compared with other spin and relativistic corrections and the observed levels do not agree closely with the Landé rule. The results for Mg, Ca, and Sr are typical of a large number of cases for which good agreement with the Landé rule is obtained. For Hg and other heavy systems the spin-orbit energy is large and departures from the Landé rule are due to partial breakdown of  $LS$  coupling. It may be noted that Hg has 80 electrons with ground configuration

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2.$$

One may also test the expression (131) for  $\zeta(n_1 l_1 n_2 l_2 L)$ . With  $l_1 + l_2 = L$  one obtains

$$\zeta(n_1 l_1 n_2 l_2 L) = \frac{1}{L} [\zeta(n_1 l_1) + \zeta(n_2 l_2)].$$

TABLE VIII  
THE LANDÉ INTERVAL RULE FOR  $nsnp\ ^3P_J$  LEVELS

	$\zeta = [^3P_1 - ^3P_0]$ (cm <sup>-1</sup> )	$\zeta = \frac{1}{2}[^3P_2 - ^3P_1]$ (cm <sup>-1</sup> )
Be 2s2p	0.68	1.18
Mg 3s3p	20.06	20.35
Ca 4s4p	52.16	52.94
Sr 5s5p	186.83	192.11
Hg 6s6p	1767.3	2315.3

In this case it is seen that  $\zeta$  should not depend on  $L$ . For C 2p3p  $^3P_J$  and  $^3D_J$  one obtains in cm<sup>-1</sup>

$$\begin{aligned}\zeta &= [^3P_1 - ^3P_0] = 12.42 & \zeta &= [^3D_2 - ^3D_1] = 10.60 \\ \zeta &= \frac{1}{2}[^3P_2 - ^3P_1] = 10.23 & \zeta &= \frac{1}{3}[^3D_3 - ^3D_2] = 11.14.\end{aligned}$$

### 11.8 Intermediate and $\eta$ Coupling

We consider the  $3pns$  series of\* Si  $1s^22s^22p^63s^23pns$ . The  $LS$  coupling electrostatic energies are given by (127) and the  $LS$  coupling spin-orbit energies by (130) with  $\zeta(3pns) = \frac{1}{2}\zeta(3p)$ . We may expect that the  $3p$  orbital will be little perturbed by the  $ns$  orbital and that  $\zeta(3p)$  will therefore be practically independent of  $n$ . The parameter  $G_1(3pns)$ , which determines the electrostatic energy separation  $[^3P - ^1P]$ , will decrease rapidly with increasing  $n$  due to the two electrons being further apart. The  $LS$  coupling approximation, which assumes the  $^3P, ^1P$  separation to be large compared with the spin-orbit energy, will therefore certainly be invalid for large  $n$ .

The observed  $3pns$  energies are plotted, relative to  $3pns\ ^3P_0$ , in Fig. 9. The levels are seen to converge to two limits. These correspond to the  $ns$  electron being removed and the Si<sup>+</sup> ion being left in the  $3p\ ^3P_{3/2}$  level or the  $3p\ ^3P_{1/2}$  level.

Off-diagonal matrix elements of the type (128) do not occur for  $J = 0$  or  $J = 2$  since the only level with  $J = 0$  is  $^3P_0$  and the only level with  $J = 2$  is  $^3P_2$ . The assumption of  $LS$  coupling therefore introduces no approximation for these values of  $J$ . The  $[^3P_2 - ^3P_0]$  separation for  $3pns$

\* We consider Si rather than C because the experimental material is more complete.

This is also the [ $^3P_{3/2} - ^3P_{1/2}$ ] separation for  $\text{Si}^+ 3p$ . That the observed [ $^3P_2 - ^3P_0$ ] separation is almost constant is therefore in good agreement with theory.

There are two states with  $J = 1$ ,  $^3P_1$  and  $^1P_1$ . The off-diagonal matrix element  $(3pns^1P_1|H_{sp}|3pns^3P_1)$  is nonzero but is neglected in  $LS$  coupling. In  $jj$  coupling one introduces the quantum numbers  $j_1$  for the  $3p$  electron and  $j_2$  for the  $ns$  electron. The states may then be labelled by the quantum numbers  $(j_1, j_2)_J$ . These states are  $(\frac{3}{2}, \frac{1}{2})_2$ ,  $(\frac{3}{2}, \frac{1}{2})_1$ ,  $(\frac{1}{2}, \frac{1}{2})_1$ , and  $(\frac{1}{2}, \frac{1}{2})_0$ . In  $jj$  coupling one neglects the off-diagonal matrix element of the electrostatic energy connecting the states  $(\frac{3}{2}, \frac{1}{2})_1$  and  $(\frac{1}{2}, \frac{1}{2})_1$ . This will be a good approximation for large  $n$ . The  $jj$  coupling labels are indicated in Fig. 9.

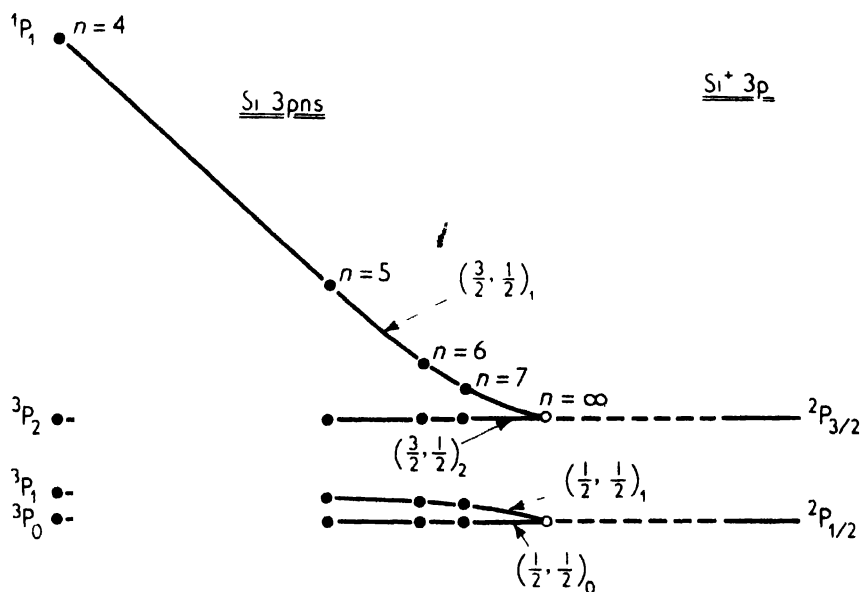


FIG. 9. The transition from  $LS$  to  $jj$  coupling. The figure shows the structure of the  $3pns$ , levels of  $\text{Si}$  for various values of  $n$ .

For intermediate values of  $n$  neither  $LS$  nor  $jj$  coupling will provide good approximations. One must consider  $J = 1$  wave functions of the type  $\{a\Psi(3pns^1P_1) + b\Psi(3pns^3P_1)\}$ , the linear combination being chosen so as to diagonalize the complete energy matrix. The four levels depend on three parameters,  $E_0, G_1$  and  $\zeta$ , so a check on the theory may be obtained. Further details of intermediate coupling calculation for  $ps$  configurations are given by Condon and Shortley,\* p. 271.

## 11.9 Configuration Interaction

It has so far been assumed that the energy of an atomic level may be calculated using wave functions belonging to a single configuration. Second-order perturbation theory (see § 6.1.) suggests that this approximation may fail when nearly equal energies are obtained for two different configurations. One must then consider wave functions which are linear combinations of the wave functions  $\Psi(I')$  and  $\Psi(I'')$  for the two configurations. *Configuration interaction* is said to be important when an appreciable admixture of these two functions occurs. A necessary condition for configuration interaction is that the matrix element  $(I'|H|I'')$  should be nonzero (see (49)). This requires that the states  $\Psi(I'), \Psi(I'')$  should have the same parity (see § 5.5.) and the same value of  $J$ ; in  $LS$  coupling it is also necessary that they should have the same values of  $S$  and  $L$ .

Configuration interactions in spectral series may often be detected by an anomalous variation of the quantum defect obtained from the Ritz formula (29). An example occurs in the  $4snd\ ^3D$  series of Ca. The levels  $4s8d$  and  $4s9d$  have energies close to the energy of  $3d5s\ ^3D$ . The whole of the  $4snd\ ^3D$  series is perturbed, the perturbation being largest for  $4s8d$  and  $9d$ .

Configuration interaction is discussed in some detail by White<sup>4</sup> (Chapter XIX) and by Condon and Shortley<sup>3</sup> (Chapter XV).

## 12. Three Electrons Outside of Closed Shells

Configurations  $n_1l_1n_2l_2n_3l_3$  containing 3 inequivalent electrons occur infrequently. We shall therefore consider only  $n_1l_1^2n_2l_2$  and  $nl^3$ .

### 12.1 Parent Terms

The wave functions for  $n_1l_1^2n_2l_2$  may be constructed in the following manner. For  $(S_1 + L_1)$  even the function  $\Psi(n_1l_1^2S_1L_1M_{S_1}M_{L_1}|\mathbf{x}_1\mathbf{x}_2)$  will be normalized and antisymmetric. We form the coupled three-electron function

$$\begin{aligned} & \psi(n_1l_1^2(S_1L_1)n_2l_2SLM_S M_L|\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_3) \\ &= \sum_{M_{S_1} m_{s_2} M_{L_1} m_{l_2}} (S_1 \frac{1}{2} M_{S_1} m_{s_2} | S_1 \frac{1}{2} S M_S) (L_1 l_2 M_{L_1} m_{l_2} | L_1 l_2 L M_L) \times \\ & \quad \Psi(n_1l_1^2S_1L_1M_{S_1}M_{L_1}|\mathbf{x}_1, \mathbf{x}_2) \psi(n_2l_2m_{s_2}m_{l_2}|\mathbf{x}_3). \end{aligned} \quad (134)$$

This function will be normalized but will not be antisymmetric for interchange of  $x_3$  with  $x_1$  or  $x_2$ . We now form the antisymmetric function

$$\Psi(x_1, x_2, x_3) = \frac{1}{\sqrt{3}} [\psi(x_1, x_2, x_3) - \psi(x_1, x_3, x_2) + \psi(x_2, x_3, x_1)]. \quad (135)$$

This will be normalized if  $P_{n_1 l_1}$  is orthogonal to  $P_{n_2 l_2}$ .

It is seen that the quantum states of the  $n_1 l_1^2 n_2 l_2$  configuration may be specified in terms of the quantum numbers  $n_1 l_1^2 (S_1 L_1) n_2 l_2 S L M_S M_L$ . Thus we could have

$$\begin{array}{ll} 2p^2(^3P)3p & ^2S, ^2P, ^2D, ^4S, ^4P, ^4D \\ 2p^2(^1D)3p & ^2P, ^2D, ^2F \\ 2p^2(^1S)3p & ^2P. \end{array}$$

Except for  $2p^2(^1D)3p^2F$  and  $2p^2(^1S)3p^2P$  these are all observed as excited states of nitrogen (ground configuration  $1s^2 2s^2 2p^3$ ). The quantum numbers  $S_1 L_1$  are said to specify the *parent term* of  $n_1 l_1^2$ . It is seen that a given set of quantum numbers  $S L M_S M_L$  is in some cases obtained from only one parent term but in other cases may be obtained from two or more different parent terms. Thus specification of a parent term may be required in order to specify a quantum state of  $n_1 l_1^2 n_2 l_2$ .

In order to obtain the electrostatic energies it is necessary to calculate the matrix elements

$$(n_1 l_1^2 (S_1 L_1) n_2 l_2 S L | H | n_1 l_1^2 (S'_1 L'_1) n_2 l_2 S L).$$

Although the off-diagonal matrix elements,  $(S_1 L_1) \neq (S'_1 L'_1)$ , may not be zero they may usually be neglected in a first approximation. The energy levels may then be specified in terms of the quantum numbers  $n_1 l_1^2 (S_1 L_1) n_2 l_2 S L$ .

In the spectrum of nitrogen one would expect to observe spectral series converging to different spectral limits, some to the  $2p^2\ ^3P$  ground state of the ion and others to the  $2p^2\ ^1D$  and  $^1S$  excited states. Fragments of such series have been observed in nitrogen and more complete development of such series is observed in several members of the nitrogen iso-electronic sequence.

## 12.2 Three Equivalent Electrons: Fractional Parentage Coefficients

As in the two-electron case the exclusion principle imposes restrictions on the values of  $S L$  which may occur in  $n l^3$  configurations. In the previous section it was shown that the terms  $^2S, ^2P, ^2D, ^2F, ^4S, ^4P$  and  $^4D$  are allowed in the  $2p^3 3p$  configuration. Of these only  $^2P, ^2D$  and  $^4S$  are allowed in  $2p^3$ .

could obtain functions

$$\psi(2p^3(S_1L_1)2pSL|x_1, x_2, x_3)$$

(136)

which would be antisymmetric for interchange of  $x_1, x_2$  but may not be antisymmetric for interchange of  $x_3$  with  $x_1$  or  $x_2$ . From (136) one could attempt to obtain an antisymmetric function using (135). One would find that for the disallowed values of  $SL$  the function obtained would be identically zero.

Let us consider the allowed  $^2D$  term of  $2p^3$ . Using (135) to antisymmetrize the function (136) one would obtain two functions,  $\Psi(2p^3(^3P)2p^2D)$  and  $\Psi(2p^3(^1D)2p^2D)$  but one would find that these two functions would not be linearly independent and would not be normalized; one would be a constant multiple of the other. In consequence the specification of parent terms,  $^3P$  and  $^1D$ , would cease to have any meaning. This is an example of a general rule: for a group of equivalent electrons the only meaningful quantum numbers are those for the group as a whole.

To obtain the normalized antisymmetric function  $\Psi(2p^3^2D|x_1, x_2, x_3)$  we may proceed as follows. The functions  $\psi(2p^3(^3P)2p^2D|x_1, x_2, x_3)$  and  $\psi(2p^3(^1D)2p^2D|x_1, x_2, x_3)$  will each contain a part which is antisymmetric for interchange of  $x_3$  with  $x_1$  or  $x_2$  and a part which is symmetric for these interchanges. We may now find a linear combination of these two functions for which the symmetric parts cancel out. If we also take the combination to be normalized it may be written

$$\Psi(2p^3^2D|x_1, x_2, x_3) = (p^2(^3P)p^2D|\}p^3^2D)\psi(2p^3(^3P)2p^2D|x_1, x_2, x_3) + \quad (137) \\ (p^2(^1D)p^2D|\}p^3^2D)\psi(2p^3(^1D)2p^2D|x_1, x_2, x_3).$$

This gives the normalized antisymmetric  $2p^3$  function. The coefficients  $(p^2(S_1L_1)pSL|\}p^3SL)$  are known as *fractional parentage coefficients*. Inserting numerical values for the coefficients Eq. (137) may be written

$$\Psi(2p^3^2D) = \frac{1}{\sqrt{2}} \psi(2p^3(^3P)2p^2D) - \frac{1}{\sqrt{2}} \psi(2p^3(^1D)2p^2D).$$

For the other  $2p^3$  terms one obtains

$$\Psi(2p^3^3P) = \frac{\sqrt{2}}{3} \psi(2p^3(^1S)2p^2P) - \frac{1}{\sqrt{2}} \psi(2p^3(^3P)2p^2P) - \frac{\sqrt{5}}{3\sqrt{2}} \psi(2p^3(^1D)2p^2P)$$

and

$$\Psi(2p^3^4S) = \psi(2p^3(^3P)2p^4S).$$

The evaluation of fractional parentage coefficients is discussed by Racah<sup>7</sup> and by Rose.<sup>8</sup> Once the coefficients are known the evaluation of matrix

elements is usually straightforward. We leave it as an exercise for the reader to show\* that the expressions for the electrostatic energies are

$$\begin{aligned} SL & E(2p^3 SL) \\ {}^2P & E_1 \\ {}^2D & E_1 - \frac{6}{25} F_2 \\ {}^4S & E_0 - \frac{15}{25} F_2. \end{aligned}$$

We obtain the ratio

$$\frac{[{}^2P - {}^2D]}{[{}^2D - {}^4S]} = \frac{2}{3}$$

The ratio observed for the  $2p^3$  configuration in nitrogen is 0.500.

Further complications arise when one considers groups of three equivalent electrons with  $l > 1$ . The term values  $SL$  then no longer suffice to give a complete specification of states; for a given  $SL$  one may have two or more linearly independent functions. Other quantum numbers must then be introduced.<sup>7</sup>

### 13. The Calculation of Atomic Wave Functions

In the preceding sections we have concentrated attention on the form of the wave functions and on the expressions for the energy. Consideration of more complicated cases would introduce nothing new. Thus the treatment of configurations with four electrons outside of closed shells follows the same lines as those considered in § 12 for three electrons.

If we wish to calculate numerical values for atomic energies a more detailed calculation of wave functions is necessary. It is this problem to which we now turn our attention.

#### 13.1 Variational Methods

We seek approximate solutions of the Schrödinger equation  $(H - E_g)\Phi_g = 0$ ,  $E_g$  being the lowest eigenvalue of  $H$ . Let  $\Psi$  be any function satisfying

$$\equiv \int \Psi^* \Psi d\tau. \quad (138)$$

\* It may be noted that, when antisymmetric functions are used, the matrix of  $(1/r_{12} + 1/r_{13} + 1/r_{23})$  is equal to the matrix of  $3/r_{12}$ .



and define  $E$  as

$$E \equiv \int \Psi^* H \Psi d\tau. \quad (138)$$

Then†  $E \geq E_g$ . The function  $\Psi$  could be of a specified analytical form containing parameters  $a_1, a_2, \dots, a_n$ . In order that  $E$  should be a good approximation to  $E_g$  we choose the parameters to be such that  $E$  is as small as possible. A necessary condition‡ is

$$\frac{\partial E}{\partial a_i} = 0, \quad 1 \leq i \leq n \quad (140)$$

(subject to the condition  $\Delta = 1$ ). More generally we may consider a variation  $\delta\Psi$  of  $\Psi$  and introduce

$$\delta E = \int (\Psi + \delta\Psi)^* H (\Psi + \delta\Psi) d\tau - \int \Psi^* H \Psi d\tau. \quad (141)$$

Then for small variations, neglecting quadratic terms in  $\delta\Psi$ ,

$$\delta E = \int \delta\Psi^* H \Psi d\tau + \int \Psi^* H \delta\Psi d\tau.$$

When the integral  $\Delta$  exists we have, by the Hermitian property of  $H$ ,

$$\delta E = \int \delta\Psi^* H \Psi d\tau + \int \delta\Psi H \Psi^* d\tau \quad (142)$$

(Vol. I, Chapter 1, § 2.2). In place of (140) we have

$$\delta E = 0 \quad (\text{all variations consistent with } \Delta = 1). \quad (143)$$

Removing the restriction that  $\Delta$  should be constant we may define

$$\begin{aligned} \delta\Delta &= \int (\Psi + \delta\Psi)^* (\Psi + \delta\Psi) d\tau - \int \Psi^* \Psi d\tau \\ &= \int \delta\Psi^* \Psi d\tau + \int \delta\Psi \Psi^* d\tau. \end{aligned} \quad (144)$$

When  $\Delta$  is constant we have  $\delta\Delta = 0$  and (143) may be written

$$\delta(E - \lambda\Delta) = 0 \quad (\text{all } \lambda, \delta\Psi \text{ such that } \Delta = 1) \quad (145)$$

† Use the expansion  $\Psi = \sum c_n \Phi_n$  where  $(H - E_n)\Phi_n = 0$ . Then  $E = \sum |c_n|^2 E_n$  and, by (138),  $\sum |c_n|^2 = 1$ . With  $E_n \geq E_g$  for all  $n$  it is evident that  $E \geq E_g$ .

‡ The condition is that  $E$  should be stationary for small variations of the parameters. We assume that the stationary condition corresponds to a minimum.

where  $\lambda$  is a number. If we remove the condition that  $\delta\Psi$  must be such that  $\delta\Delta = 0$ , the equation  $\delta(E - \lambda\Delta) = 0$  gives an equation for  $\Psi$  which includes the parameter  $\lambda$ . For arbitrary  $\lambda$  the solutions of this equation may be such that the integral  $\Delta$  does not exist. In place of (145) we therefore take the condition

$$\delta(E - \lambda\Delta) = 0 \quad (\text{all } \delta\Psi, \lambda \text{ such that } \Delta \text{ exists}). \quad (146)$$

This is the method of *Lagrange multipliers*.<sup>14</sup> From (142) and (144) we obtain

$$\int \delta\Psi^*(H - \lambda)\Psi d\tau + \int \delta\Psi(H - \lambda)\Psi^* d\tau = 0. \quad (147)$$

Since the real and imaginary parts of  $\Psi$  may be varied independently,  $\delta\Psi$  and  $\delta\Psi^*$  may be considered to be independent quantities. If (147) is to be satisfied for all variations we must have

$$\int \delta\Psi^*(H - \lambda)\Psi d\tau \quad \text{and} \quad \int \delta\Psi(H - \lambda)\Psi^* d\tau = 0. \quad (148)$$

These equations can be satisfied for all variations  $\delta\Psi, \delta\Psi^*$  only if  $(H - \lambda)\Psi = (H - \lambda)\Psi^* = 0$  and the integral  $\Delta$  will exist only if  $\lambda$  is an eigenvalue of  $H$ . The conditions (146) for unrestricted variations is thus seen to be equivalent to the condition that  $\Psi$  should be an eigenfunction of the Schrödinger equation.

With functions  $\Psi$  of prescribed functional form it may not be possible to solve this Schrödinger equation. In its place we may solve (146) for all  $\delta\Psi$  consistent with the prescribed functional form.

### 13.2 Simple Analytic Functions for He

An approximate ground state function is  $\psi = A \exp[-a(r_1 + r_2)]$ . With  $A = a^3/\pi$  this is normalized for all  $a$  and the variational condition is  $(\partial E/\partial a) = 0$ . One obtains†  $a = 27/16$  and  $E = -(27/16)^2 = -2.848$  atomic units. The observed energy is  $E_g = -2.904$  atomic units.

We consider next the lowest triplet state,  $1s2s\ ^3S$ . A symmetrized function of type (78) may be used together with analytic radial functions

$$P_{1s} = A r e^{-a_1 r}, \quad P_{2s} = B r \{e^{-a_2 r} - C r e^{-a_3 r}\}. \quad (149)$$

† Details of the calculation are given by Hartree,<sup>10</sup> p. 33.

From (94) the energy expression is

$$E = I(1s) + I(2s) + F_0(1s2s) - G_0(1s2s)$$

provided that

$$\int_0^\infty P_{1s}^2 dr = 1, \quad \int_0^\infty P_{2s}^2 dr = 1, \quad \int_0^\infty P_{1s} P_{2s} dr = 0.$$

Using these conditions we may express  $A$ ,  $B$  and  $C$  in terms of  $a_1, a_2, a_3$ . The variational condition is then  $(\partial E / \partial a_i) = 0$  ( $i = 1, 2, 3$ ). One obtains<sup>21</sup>  $a_1 = 2.00$ ,  $a_2 = 1.57$ ,  $a_3 = 0.61$ . The wave functions may then be used to calculate the energies of  $1s2s\ ^3S$  and of  $1s2s\ ^1S$  with the results shown in Table IX.

TABLE IX  
ENERGIES IN ATOMIC UNITS (27 20 ev)

		Calculated		Observed	
He	$1s2s\ ^1S$	- 2.148		- 2.146	
	$1s2s\ ^3S$	- 2.174	- 0.026	- 2.175	- 0.029

It should be noted that the variational methods described in § 13.1, if applied without additional subsidiary conditions, automatically give approximate ground state wave functions. In the He  $1s2s\ ^3S$  calculations we impose the condition that the spatial function should be antisymmetric. The variational method then gives an approximate wave function for the lowest triplet state. Improved radial functions of type (149) for  $1s2s\ ^1S$  are obtained if the condition  $\int P_{1s} P_{2s} dr = 0$  is not imposed but the condition is imposed that the complete wave function should be orthogonal to a  $1s^2\ ^1S$  function.<sup>15</sup>

Further references to He variational calculations are given by Hartree.<sup>10</sup>

### 13.3 The Hartree-Fock Method: General Theory

We consider states which may be represented by single  $D$ -functions (§ 10.1) and write  $i$  for the set of quantum numbers  $\alpha_i$  and  $\varphi_i(\mathbf{x})$  for  $\varphi(\alpha_i|\mathbf{x})$ .

The variational method is used to determine the functions  $\varphi_i$ . From § 10.3 we obtain, in atomic units,

$$E = \sum_i I(i) + \sum_{ij}' \left\{ \left( ij \left| \frac{1}{r_{12}} \right| ij \right) - \left( ij \left| \frac{1}{r_{12}} \right| ji \right) \right\} \quad (150)$$

where

$$\begin{aligned} I(i) &= \int \varphi_i^*(\mathbf{x}_1) H_1(\mathbf{x}_1) \varphi_i(\mathbf{x}_1) d\mathbf{x}_1 \\ H_1(\mathbf{x}_1) &= -\frac{1}{2} \nabla_1^2 - \frac{Z}{r_1} \\ ij \left| \frac{1}{r_{12}} \right| kl &= \iint \varphi_i^*(\mathbf{x}_1) \varphi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \varphi_k(\mathbf{x}_1) \varphi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned}$$

In the derivation of (150) it is assumed that

$$\int \varphi_i^*(\mathbf{x}) \varphi_j(\mathbf{x}) d\mathbf{x} \equiv (i|j) = \delta_{ij}.$$

The condition  $\delta E = 0$  must therefore be imposed subject to the condition  $(i|j) = \delta_{ij}$ . Generalizing the method of § 13.1 we impose the condition

$$\delta \left[ E - \sum_{ij} \lambda_{ij} (i|j) \right] = 0 \quad (\lambda_{ij} = \lambda_{ji}) \quad (151)$$

for all variations of the orbitals  $\varphi_i$ . We then have  $\frac{1}{2}N(N+1)$  parameters  $\lambda_{ij}$  which may be adjusted in order to satisfy the  $\frac{1}{2}N(N+1)$  conditions  $(i|j) = \delta_{ij}$ . For variation of  $\varphi_i^*(\mathbf{x}_1)$  we have

$$\begin{aligned} \delta I(i) &= \delta \varphi_i^*(\mathbf{x}_1) H_1 \varphi_i(\mathbf{x}_1) d\mathbf{x}_1 \\ \delta \left( ij \left| \frac{1}{r_{12}} \right| kl \right) &= \iint \delta \varphi_i^*(\mathbf{x}_1) \varphi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \varphi_k(\mathbf{x}_1) \varphi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ \delta (i|j) &= \int \delta \varphi_i^*(\mathbf{x}_1) \varphi_j(\mathbf{x}_1) d\mathbf{x}_1. \end{aligned}$$

Introducing -

$$v_{ji}(\mathbf{x}_1) = \int \varphi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \varphi_i(\mathbf{x}_2) d\mathbf{x}_2$$

we have

$$ij \left| \frac{1}{r_{12}} \right| kl = \int \delta \varphi_i^*(\mathbf{x}_1) v_{ji}(\mathbf{x}_1) \varphi_k(\mathbf{x}_1) d\mathbf{x}_1.$$

For variation of  $\varphi_i^*$  Eq. (151) therefore gives

$$\delta \left[ E - \sum_i \lambda_i (i|i) \right] = \int \delta \varphi_i^* \left[ H_1 \varphi_i + \sum_j (v_{jj} \varphi_i - v_{ji} \varphi_j) - \sum_j \lambda_j \varphi_j \right] d\mathbf{x}_1 = 0$$

For this to be satisfied for all variations  $\delta \varphi_i^*$  we must have

$$H_1 \varphi_i + \sum_j (v_{jj} \varphi_i - v_{ji} \varphi_j) - \sum_j \lambda_j \varphi_j = 0. \quad (152)$$

These are the Hartree-Fock equations.

### 13.4 The Hartree Self-Consistent Field

If, in (152), we omit all  $v_{ji}$  and  $\lambda_j$  for  $j \neq i$  we obtain

$$\left( H_1 + \sum_{j \neq i} v_{jj} - \lambda_{ii} \right) \varphi_i = 0. \quad (153)$$

These equations would have been obtained if we had applied the variational method to unsymmetrized functions  $\psi = \varphi_1(\mathbf{x}_1) \varphi_2(\mathbf{x}_2) \dots \varphi_N(\mathbf{x}_N)$ . They are the self-consistent field equations already obtained by a more physical argument in § 2.2. The  $\lambda_{ii}$ , which are equal to the one-electron energies  $E_i$  occurring in the central field model, must be adjusted to obtain solutions for which  $(i|i)$  exists.

The complete equations (152), with the exchange terms  $v_{ji}$ , were first obtained by Fock using a variational argument.

### 13.5 The Hartree-Fock Radial Equations

The equations (152) are not in a form suitable for numerical calculations. The practical procedure is to express the energy  $E$  in terms of integrals over radial functions. In obtaining the expression for  $E$  it is usually assumed that

$$(nl|n'l) \equiv \int_0^\infty P_{nl}(r) P_{n'l}(r) dr = \delta_{nn'}. \quad (154)$$

The variational expression is therefore

$$\delta \left[ E + \frac{1}{2} \sum_{nn'l} \varepsilon_{n'l, nl} (nl|n'l) \right] = 0. \quad (155)$$

From the expression (111) for the energy of  $\text{Na}^+1s^22s^22p^6$  the reader may obtain the equations\* for  $P_{1s}(r)$ ,  $P_{2s}(r)$  and  $P_{2p}(r)$ :

$$\begin{aligned} \left[ \frac{d^2}{dr^2} + u + 2\gamma_0(1s1s) - \varepsilon_{1s,1s} \right] P_{1s} &= -2\gamma_0(1s2s)P_{2s} - 2\gamma_1(1s2p)P_{2p} + \varepsilon_{1s,2s}P_{2s}, \\ \left[ \frac{d^2}{dr^2} + u + 2\gamma_0(2s2s) - \varepsilon_{2s,2s}P_{2s} \right] &= -2\gamma_0(1s2s)P_{1s} - 2\gamma_1(2s2p)P_{2p} + \varepsilon_{1s,2s}P_{1s}, \\ \left[ \frac{d^2}{dr^2} - \frac{2}{r^2} + u + 2\gamma_0(2p2p) + \frac{4}{5}\gamma_2(2p2p) - \varepsilon_{2p,2p} \right] P_{2p} \\ &= -\frac{2}{3} \sum_{n'=1,2} \gamma_1(n's2p)P_{n's} \end{aligned}$$

where  $\gamma_\lambda(nln'l'|r)$  is defined by (88) and where

$$u(r) = 2 \left[ \frac{11}{r} - 2 \sum_{n'=1,2} \gamma_0(n'sn's) - 6\gamma_0(2p2p) \right].$$

For an  $nl$  valence electron of Na the radial equation is

$$\begin{aligned} \left[ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + u(r) - \varepsilon_{nl,nl} \right] P_{nl} &= \sum_{n'=1,2} \left[ \frac{-2}{(2l+1)} \gamma_l(n'snl) + \delta_{l0}\varepsilon_{n's,ns} \right] P_{n's} - \\ &3 \sum C_{1nl}\gamma_\lambda(2pnl)P_{2p} + \delta_{l1}\varepsilon_{2p,np}P_{2p}. \end{aligned}$$

TABLE X  
Na VALENCE-ELECTRON ENERGIES IN UNITS OF 13 60 ev

$nl$	Hartree equations	Hartree-Fock equations	Experiment
3s	0.316	0.360	0.378
3p	0.178	0.219	0.223
4s	0.128	0.141	0.143
4p	0.088	0.100	0.102

\* The derivation of these equations is described fully by Hartree,<sup>10</sup> p. 55.

The corresponding self-consistent field equations are obtained on omitting all exchange terms  $\gamma_\lambda(nln'l')$  and  $\varepsilon_{nln'l'}$  with  $nl \neq n'l'$  and also all terms  $\gamma_\lambda(nlnl)$  with  $\lambda > 0$ .

Solutions of the equations have been obtained<sup>16</sup> with the usual approximation of neglecting perturbation of the  $\text{Na}^+$  core by the valence electron. Substitution of the solutions in the expression for the energy shows that  $\varepsilon_{nl,ni}$  is equal to the energy required to remove the valence electron, measured in units of 13.60 ev. The calculated energies are compared with experimental energies in Table X.

## 14. Radiative Transition Probabilities

### 14.1 Electric Dipole Radiation

An atom in an excited state  $a$  may undergo a spontaneous radiative transition to a lower state  $b$ , the quantum emitted having energy  $h\nu = (E_b - E_a)$  and wavelength  $\lambda = c/\nu$ . For electric dipole radiation (Vol I, Chapter 8, § 5.1.4) the transition probability is

$$A(a \rightarrow b) = \frac{64\pi^4}{3h\lambda^3} S(b,a) \quad (156)$$

where

$$S(b,a) = e \sum (b|\mathbf{r}_i|a) \quad (157)$$

It should be noted that  $S(b,a) = S(a,b)$ .

One is usually interested in transitions between two energy levels. Let the upper level  $a$  have a number  $\omega_a$  of quantum states  $\psi(a_i)$  and let the lower level  $b$  have a number  $\omega_b$  of quantum states  $\psi(b_j)$ . The numbers  $\omega_a, \omega_b$  are the *statistical weights* of the two levels. Assuming equal population probabilities for the upper states, the transition probability is calculated on summing over all final states and averaging over all upper states. One obtains

$$A(a \rightarrow b) = \frac{64\pi^4}{3h\lambda^3} \cdot \frac{1}{\omega_a} \cdot S(b,a)$$

with

$$S(b,a) = \sum_{i,j} S(b_j,a_i). \quad (158)$$

## 14.2 The Dipole Moment

The vector  $-e(a|\mathbf{r}|b)$  is the dipole moment for the transition.\* By definition

$$|(b|\mathbf{r}|a)|^2 = |(b|x|a)|^2 + |(b|y|a)|^2 + |(b|z|a)|^2$$

and therefore

$$|(b|\mathbf{r}|a)|^2 = \frac{1}{2}|(b|x + iy|a)|^2 + \frac{1}{2}|(b|x - iy|a)|^2 + |(b|z|a)|^2.$$

Using  $(x + iy) = r(\sin \theta)e^{i\varphi}$ ,  $(x - iy) = r(\sin \theta)e^{-i\varphi}$  and  $z = r \cos \theta$ , the expression (21) for the normalized spherical harmonic  $Y_{1\mu}(\hat{\mathbf{r}})$  and the definition  $C_{1\mu} = (4\pi/3)^{1/2}Y_{1\mu}$ , one obtains

$$|(b|\mathbf{r}|a)|^2 = \sum_{\mu} |(b|rC_{1\mu}(\hat{\mathbf{r}})|a)|^2. \quad (159)$$

## 14.3 Electric Quadrupole Radiation and Magnetic Dipole Radiation

The expression for the electric dipole transition probability is obtained on neglecting the spatial variation of the electric vector of the radiation field in the vicinity of the atom, and neglecting interactions between the atom and the magnetic vector of the radiation field. When these approximations are not made one obtains finite probabilities for the emission of electric quadrupole radiation and magnetic dipole radiation. The quadrupole transition probability is

$$A_q(a \rightarrow b) = \frac{32\pi^6}{3h\lambda^5} S_q(b, a) \quad (160)$$

with

$$S_q(b, a) = e^2 \frac{2}{3} \sum_i \sum_{\mu} |(b|r_i^2 C_{2\mu}(\hat{\mathbf{r}}_i)|a)|^2 \quad (161)$$

and the magnetic dipole transition probability is

$$A_m(a \rightarrow b) = \frac{64\pi^4}{3h\lambda^3} S_m(b, a) \quad (162)$$

with

$$S_m(b, a) = \frac{e}{2mc} |(b|\mathbf{L} + 2\mathbf{S}|a)|^2 \quad (163)$$

\* For simplicity we here consider only one electron.



Assuming that  $S$  and  $S_q$  will both be of order unity when expressed in atomic units one sees that  $A_q/A$  will be of order  $(a_0/\lambda)^2 \approx 10^{-6}$ . One might assume that  $S_m$  would be of order  $(2 \times 137)^{-2}$  when expressed in atomic units giving  $(A_m/A) \sim 10^{-5}$ . In practice  $S_m$  will be a good deal smaller due to the operation of selection rules. Generally speaking  $A_q$  and  $A_m$  are of comparable order of magnitude and are smaller than dipole transition probabilities by factors of order  $10^{-6}$ . It may happen, however, that the dipole transition probability vanishes identically and in such cases  $A_q$  and  $A_m$  may be of importance.

#### 14.4 Spin, Parity, and Configuration Selection Rules

The operators in the electric dipole and quadrupole matrix elements do not operate on spin coordinates. From the orthonormality of the total spin functions one obtains the selection rule

$$\Delta S = 0 \quad (\text{electric multipole transitions}). \quad (164)$$

This rule does not apply to magnetic multipole transitions.

The operator  $\sum \mathbf{r}_i$  for electric dipole transitions is of odd parity. For a nonvanishing matrix element the initial and final atomic states must therefore have opposite parity (see § 5.3): the selection rule is

$$(\text{even parity}) \nleftrightarrow (\text{odd parity}) \quad (\text{electric dipole transitions}). \quad (165)$$

For electric quadrupole and magnetic dipole transitions the rule is that the atomic parity does *not* change.

Certain configuration selection rules may be deduced from the fact that all radiative matrix elements are of the type

$$\sum_i (b|f(\mathbf{x}_i)|a).$$

With two-electron states

$$\psi(\alpha_1\alpha_2|\mathbf{x}_1,\mathbf{x}_2) = \varphi(\alpha_1|\mathbf{x}_1)\varphi(\alpha_2|\mathbf{x}_2)$$

$$\psi(\beta_1\beta_2|\mathbf{x}_1,\mathbf{x}_2) = \varphi(\beta_1|\mathbf{x}_1)\varphi(\beta_2|\mathbf{x}_2)$$

one obtains

$$\sum_i (\beta_1\beta_2|f(\mathbf{x})|\alpha_1\alpha_2) = (\beta_1|f|\alpha_1)(\beta_2|\alpha_2) + (\beta_1|\alpha_1)(\beta_2|f|\alpha_2). \quad (166)$$

Making the usual assumption that  $(\beta_i|\alpha_i)$  is zero for  $\beta_i \neq \alpha_i$ , we see that (166) will be zero if  $\beta_1$  is not equal to  $\alpha_1$  and at the same time  $\beta_2$  not equal

to  $\alpha_2$ . Also, due to the parity rule, the electric dipole matrix element will vanish if both  $\beta_1 = \alpha_1$  and  $\beta_2 = \alpha_2$ . Therefore  $(\beta_1\beta_2|r_1 + r_2|\alpha_1\alpha_2)$  may be nonzero only if  $\beta_1 = \alpha_1$  and  $\beta_2 \neq \alpha_2$  or if  $\beta_1 \neq \alpha_1$  and  $\beta_2 = \alpha_2$ . For electric quadrupole and magnetic dipole transitions nonzero matrix elements may also occur for  $\beta_1 = \alpha_1$  and  $\beta_2 = \alpha_2$ .

The above argument may be generalized to the case of antisymmetric many-electron states. For electric dipole transitions the usual formulation of the rule is that only one-electron jumps occur; the initial and final configurations differ by the configuration of one-electron only. For electric quadrupole radiation the rules are that one-electron jumps or the configuration remains unchanged. For magnetic dipole radiation the rule is that the configuration does not change.

### 14.5 The One-Electron Electric Dipole Moment

We first evaluate  $(nlm|z|n'l'm')$ . Putting  $z = r \cos \theta$  we have

$$(nlm|z|n'l'm') = (lm|\cos \theta|l'm')(nl|r|n'l')$$

where

$$(nl|r|n'l') = \int_0^\infty P_{nl}(r)rP_{n'l'}(r) dr. \quad (167)$$

The matrix element  $(lm|\cos \theta|l'm')$  vanishes unless  $m = m'$ . We therefore consider

$$(lm|\cos \theta|l'm) = \int Y_{lm}^*(\hat{r}) \cos \theta Y_{l'm}(\hat{r}) d\hat{r}. \quad (168)$$

The recurrence relation<sup>17</sup>

$$(2l+1)tP_l^m(t) = (l+m)P_{l-1}^m(t) + (l-m+1)P_{l+1}^m(t) \quad (169)$$

satisfied by associated Legendre polynomials gives the recurrence relation

$$\cos \theta Y_{lm} = \left[ \frac{l^2 - m^2}{4l^2 - 1} \right]^{1/2} Y_{l-1,m} + \left[ \frac{(l+1)^2 - m^2}{4(l+1)^2 - 1} \right]^{1/2} Y_{l+1,m} \quad (170)$$

satisfied by normalized spherical harmonics. Substitution of (170) in (168) gives the selection rule  $\Delta l = \pm 1$ . For  $l' = l - 1$  one obtains

$$(lm|\cos \theta|l-1,m) = \left[ \frac{l^2 - m^2}{4l^2 - 1} \right]^{1/2}. \quad (171)$$

The matrix elements of  $(x \pm iy)$  may be evaluated in a similar way using the recurrence relation<sup>17</sup>

$$(2l+1)(1-i^2)^{1/2}P_l^m = P_{l+1}^{m+1} - P_{l-1}^{m+1}. \quad (172)$$

The selection rules for  $(nlm|r|n'l'm')$  are

$$\Delta m = 0, \pm 1 \quad \text{and} \quad \Delta l = \pm 1. \quad (173)$$

The final expression obtained for

$$S(nl, n'l-1) = e^2 \sum_{mm'} |(nlm|r|n'l-1m')|^2$$

is

$$S(nl, n'l-1) = l|(nl|r|n'l-1)|^2. \quad (174)$$

#### 14.6 Selection Rules for $S$ , $L$ , and $J$

These rules may be deduced using the commutation relations<sup>8</sup> and matrix algebra or, what is effectively the same thing, using tensor operator methods.<sup>8,9</sup> We shall give the rules without proof.

*Electric dipole radiation*

$$\Delta S = 0; \quad \Delta L = 0, \pm 1 \text{ (not } 0 \rightarrow 0\text{)}; \quad \Delta J = 0, \pm 1 \text{ (not } 0 \rightarrow 0\text{)}.$$

*Electric quadrupole radiation*

$$\Delta S = 0; \quad \Delta L = 0, \pm 1, \pm 2 \text{ (not } 0 \rightarrow 0\text{)}; \quad \Delta J = 0, \pm 1, \pm 2 \\ \text{(not } 0 \rightarrow 0, \frac{1}{2} \rightarrow \frac{1}{2}, 0 \rightleftharpoons 1\text{)}.$$

*Magnetic dipole radiation*

$$\Delta S = 0; \quad \Delta L = 0; \quad \Delta J = 0, \pm 1 \text{ (not } 0 \rightarrow 0\text{)}.$$

#### 14.7 Relative Intensities

The totality of lines in the transitions between levels  $\gamma SLJ, \gamma' S' L' J'$  of two terms  $\gamma SL, \gamma' S' L'$  are said to constitute a multiplet. The relative intensities of these lines may be calculated if one assumes that the radial functions are independent of  $J, J'$ . It may be shown\* that

$$S(\gamma SLJ, \gamma' S' L' J') = \frac{(2J+1)(2J'+1)}{(2S+1)} W^2(LL'JJ'; 1S) S(\gamma SL, \gamma' S' L') \quad (175)$$

\* See Condon and Shortley,<sup>8</sup> p. 238. A straightforward proof of these relations may be obtained using (159) and standard tensor operator methods.<sup>8,9</sup>

TABLE XI  
EXPRESSIONS<sup>a</sup> FOR  $(2J+1)(2J'+1)W^2(LL'JJ';1S)$

$L'$	$J'$	$(2J+1)(2J'+1)W^2(LL'JJ';1S)$
$L-1$	$J-1$	$\frac{(J+1)(S+L+J+1)(S+L+J)(-S+L+J)(-S+L+J-1)}{4L(4L^2-1)J(J+1)}$
	$J$	$\frac{(2J+1)(S+L+J+1)(-S+L+J)(S-L+J+1)(S+L-J)}{4L(4L^2-1)J(J+1)}$
	$J+1$	$\frac{J(S-L+J+2)(S-L+J+1)(S+L-J)(S+L-J-1)}{4L(4L^2-1)J(J+1)}$
	$J-1$	$\frac{(J+1)(S+L+J+1)(-S+L+J)(S-L+J)(S+L-J+1)}{4L(L+1)(2L+1)J(J+1)}$
	$J$	$\frac{(2J+1)[L(L+1)+J(J+1)-S(S+1)]^2}{4L(L+1)(2L+1)J(J+1)}$
	$J+1$	$\frac{J(S+L+J+2)(-S+L+J+1)(S-L+J+1)(S+L-J)}{4L(L+1)(2L+1)J(J+1)}$

<sup>a</sup> Note that  $W^2(LL'JJ';1S) = W^2(L'LJ'J;1S)$ .

where the function†  $W^2(LL'JJ';1S)$  is given in Table XI. From the definition of  $W^2$  it follows that

$$\sum_J \mathfrak{s}(\gamma SLJ, \gamma' SL'J') = \frac{(2J'+1)}{(2S+1)(2L'+1)} \mathfrak{s}(\gamma SL, \gamma' SL') \quad (176)$$

$$\sum_{J'} \mathfrak{s}(\gamma SLJ, \gamma' SL'J') = \frac{(2J+1)}{(2S+1)(2L+1)} \mathfrak{s}(\gamma SL, \gamma' SL') \quad (177)$$

and since  $\sum_J (2J+1) = (2S+1)(2L+1)$  it follows that

$$\sum_{JJ'} \mathfrak{s}(\gamma SLJ, \gamma' SL'J') = \mathfrak{s}(\gamma SL, \gamma' SL') \quad (178)$$

which is a special case of (158). Equations (176), (177) express the sum rules of Ornstein, Burger and Dorgelo: the sum of the intensities of all

Q

†  $W(abcd;ef)$  is a Racah coefficient.<sup>7,8,9,22</sup>

the lines of a multiplet which belong to the same initial or final level is proportional to the statistical weight  $((2J + 1)$  or  $(2J' + 1))$  of the initial or final level concerned.

The predicted relative intensities agree with observations for many cases but there are occasional exceptions.\*

#### 14.8 The Matrix Elements of the Dipole Length and of the Dipole Momentum

We define  $\mathbf{R} = \sum_i \mathbf{r}_i$  and  $\mathbf{P} = \sum_i \mathbf{p}_i$  with  $\mathbf{p}_i = -i\hbar\nabla_i$ . Radiative transitions have been seen to depend on the dipole length matrix elements  $(\Gamma|\mathbf{R}|\Gamma')$ . For a classical simple harmonic oscillator,  $\mathbf{R}(t) = \mathbf{R}_0 e^{i\omega t}$ , the momentum is  $\mathbf{P} = m\dot{\mathbf{R}} = m\omega\mathbf{R}$ . Putting  $\hbar\omega = (E_{\Gamma} - E_{\Gamma'})$  we obtain

$$(\Gamma|\mathbf{P}|\Gamma') = \frac{m(E_{\Gamma} - E_{\Gamma'})}{\hbar} (\Gamma|\mathbf{R}|\Gamma'). \quad (179)$$

A quantum mechanical proof of this relation is obtained using the commutation relation†

$$\mathbf{R}\mathbf{P}^2 - \mathbf{P}^2\mathbf{R} = 2i\hbar\mathbf{P}.$$

Since  $H = (1/2m)\mathbf{P}^2 + V$  this gives us

$$\mathbf{R}H - H\mathbf{R} = \frac{i\hbar}{m} \mathbf{P}$$

and therefore

$$(\Gamma|\mathbf{R}H - H\mathbf{R}|\Gamma') = (E_{\Gamma'} - E_{\Gamma})(\Gamma|\mathbf{R}|\Gamma') = \frac{i\hbar}{m} (\Gamma|\mathbf{P}|\Gamma')$$

which is equivalent to (179).

It should be noted that the identity (179) may not be satisfied if approximate wave functions are used to calculate the matrix elements.

#### 14.9 The $\delta$ -Sum Rule

With  $N$  coordinates  $\mathbf{r}$ , we obtain the commutation relation‡

$$\mathbf{R} \cdot \mathbf{P} - \mathbf{P} \cdot \mathbf{R} = 3i\hbar N.$$

\* See White<sup>4</sup> and Condon and Shortley,<sup>8</sup> p. 376.

† This is readily obtained from  $x_i p_{x_i} - p_{x_i} x_i = i\hbar$ .

‡ Again using  $x_i p_{x_i} - p_{x_i} x_i = i\hbar$ .

We calculate the diagonal matrix element  $\langle \Gamma | \mathbf{R} \cdot \mathbf{P} - \mathbf{P} \cdot \mathbf{R} | \Gamma \rangle$  using the usual expression for the matrix of the product of two operators (Vol. I, Chapter 1, Eq. 15) and obtain

$$\langle \Gamma | \mathbf{R} \cdot \mathbf{P} - \mathbf{P} \cdot \mathbf{R} | \Gamma \rangle = \sum_{\Gamma'} \{ \langle \Gamma | \mathbf{R} | \Gamma' \rangle \cdot \langle \Gamma' | \mathbf{P} | \Gamma \rangle - \langle \Gamma | \mathbf{P} | \Gamma' \rangle \cdot \langle \Gamma' | \mathbf{R} | \Gamma \rangle \} = 3i\hbar N.$$

Use of (179), together with  $\langle \Gamma' | \mathbf{P} | \Gamma \rangle = \langle \Gamma | \mathbf{P} | \Gamma' \rangle^*$  and  $\langle \Gamma' | \mathbf{R} | \Gamma \rangle = \langle \Gamma | \mathbf{R} | \Gamma' \rangle^*$ , gives

$$N = \frac{2m}{3\hbar^2} \sum_{\Gamma'} (E_{\Gamma'} - E_{\Gamma}) |\langle \Gamma | \mathbf{R} | \Gamma' \rangle|^2 \quad (180)$$

The *oscillator strength* (or *f* value) for the  $\Gamma \rightarrow \Gamma'$  transition is defined to be

$$f(\Gamma', \Gamma) = \frac{2m}{3\hbar^2} (E_{\Gamma'} - E_{\Gamma}) |\langle \Gamma | \mathbf{R} | \Gamma' \rangle|^2 = \frac{2m}{3e^2\hbar^2} (E_{\Gamma'} - E_{\Gamma}) S(\Gamma', \Gamma). \quad (181)$$

The *f* sum rule is then

$$\sum_{\Gamma'} f(\Gamma', \Gamma) = N.$$

For transitions between degenerate levels the *f* value is defined by

$$f(a', a) = \frac{2m}{3e^2\hbar^2 \omega_a} (E_{a'} - E_a) S(a', a) \quad (182)$$

and the sum rule is

$$\sum_{a'} f(a', a) = N. \quad (183)$$

It should be noted that  $f(a', a)$  is a dimensionless number but that  $f(a', a)$  is *not* equal to  $f(a, a')$ .

The *f* sum rule is of importance in connection with classical and quantum-mechanical dispersion theory.

The sum rule (183) refers to all transitions from a given level; it will not be satisfied unless all transitions involving inner (X-ray) electrons are taken into account. On the central field model one would obtain a sum of unity for all transitions involving only a valence electron. In practice one finds that the sum of *f* values for all valence-electron transitions is close to unity but is not necessarily exactly unity.

Absolute transition probabilities are required in many physical and astrophysical problems. It is not always practicable to determine experimentally the values required but in such cases calculation of transition probabilities may be possible. It is, of course, desirable to compare measured and calculated values for as many cases as possible.

Calculation of transition probabilities involves evaluation of the radial integrals  $(nl|r|n'l')$  (Eq. 167). These may be sensitive to the form of the radial functions  $P_n(r)$ . Solution of the Hartree-Fock equations gives the following results for the first two principal series lines of Na: (Table XII).

TABLE XII

	Hartree-Fock	Experiment
$f(3p, 3s)$	1.04	$1.02 \pm 0.03$
$f(4p, 3s)$	0.014	0.014

In other cases the Hartree-Fock method may not give such good results. In Ca, for example, allowance must be made for configuration interaction.

For further information on transition probability calculations the papers of Bates and Damgaard<sup>18</sup> and of Garstang<sup>19</sup> may be consulted.

### 14.11 Forbidden Lines

"Forbidden" lines are those which violate the selection rules for electric dipole radiation. We consider a few typical examples.

In the spectrum of Hg one of the strongest lines is  $6s6p\ ^3P_1 \rightarrow 6s^2\ ^1S_0$ . This violates the selection rule  $\Delta S = 0$ ; such lines are said to be *intercombination lines*. The transition  $^3P_2 \rightarrow ^1S_0$  and  $^3P_0 \rightarrow ^1S_0$  are not observed so there are no violations of the selection rules for  $J$ . It has already been seen in § 11.7 that the  $^3P$  levels are not in good agreement with the Landé interval rule and that there are therefore appreciable departures from  $LS$  coupling. The wave function for the level labelled  $^3P_1$  should be taken to be a linear combination of the  $LS$  coupling functions for  $6s6p\ ^1P_1$  and  $6s6p\ ^3P_1$ . The amount of admixture of these two functions may be deduced from the energy levels. The relative electric dipole transition probabilities for  $^1P_1 \rightarrow ^1S_0$  and  $^3P_1 \rightarrow ^1S_0$ , calculated with the admixed wave function, are in good agreement with observation. When intercombination lines occur due to

departures from  $LS$  coupling one says that  $S$  is not a "good" quantum number.

In the spectrum of Na one observes very weak absorption lines corresponding to  $s \rightarrow d$  transitions. These are due to electric quadrupole radiation. The intensities of these lines are in satisfactory agreement with theory.

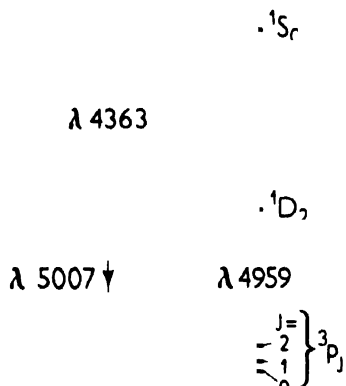


FIG. 10. The forbidden lines in the configuration  $0^{+2}1s^22s^22p^2$ . The transition  $^1S_0 \rightarrow ^1D_2$  is allowed for electric quadrupole radiation. The transitions  $^1D_2 \rightarrow ^3P_J$  occur in consequence of departures from  $LS$  coupling,  $^1D_2 \rightarrow ^3P_2$  and  $^1D_2 \rightarrow ^3P_1$  being mainly due to magnetic dipole radiation. The transition  $^1D_2 \rightarrow ^3P_0$  violates the magnetic dipole selection rule  $\Delta J = 0, \pm 1$  and has a much smaller probability.

Many lines observed in gaseous nebulae, in auroras, and in the night air-glow are due to atomic transitions which involve no configuration change. For such transitions dipole radiation is rigorously forbidden by the parity rule. Figure 10 shows the energy level diagram for the  $0^{+2}$  lines which are the strongest of all emission features in many nebulae. The  $0^{+2}$  ion is iso-electronic with C and has a  $2p^2$  ground configuration with spectral terms  $^3P, ^1D$  and  $^1S$ . The  $^1S \rightarrow ^1D$  transition is allowed for electric quadrupole radiation but the intercombination  $^1D \rightarrow ^3P$  transition is forbidden in  $LS$  coupling for both electric quadrupole and magnetic dipole transitions. When allowance is made for departures from  $LS$  coupling for  $0^{+2} ^1D \rightarrow ^3P$  it turns out that the magnetic dipole transition probability is larger than the electric quadrupole probability. The best calculated transition

probabilities<sup>20</sup> are  $A(^1S \rightarrow ^1D) = 1.6 \text{ sec}^{-1}$  and  $A(^1D \rightarrow ^3P) = 0.028 \text{ sec}^{-1}$ ; these may be compared with transition probabilities of order  $10^{-6} \text{ sec}^{-1}$  for strong electric dipole lines.







# 2. Group Theory

S. L. Altmann

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Group theory is a branch of pure mathematics which can be applied to problems as diverse as the theory of equations and the structure of crystals. This is so because it can be developed with reference to purely abstract entities only, which can later on be correlated with concrete ones, such as permutations of variables or symmetry operations. This is not, however, the course we shall take in this chapter, as we shall have in mind the applications of group theory to quantum mechanics.\* Therefore, we shall start by considering concrete entities so as to construct our group theoretical ideas around them. Since many of the applications of group theory to quantum mechanics are based on the properties of symmetry operations, we shall use these to provide a concrete background to our discussion.

\* A fuller account of these applications will be found in the references<sup>1-6</sup> at the end of this chapter. Wigner<sup>1</sup> is still the most complete treatment available and much of it has been used in this chapter. Murnaghan<sup>7</sup> gives a more mathematical treatment, with some applications to quantum theory. General mathematical books on group theory are listed in references.<sup>8-11</sup> Speiser<sup>8</sup> is probably the most useful treatment available as a background for later applications to physics and chemistry. Chapters on applied group theory are included in the books listed in references.<sup>12-16</sup> Burckhardt<sup>12</sup> gives a group-theoretical account of space and point groups in crystals. Useful review articles are those of Eckart<sup>17</sup> (general applications), Rosenthal and Murphy<sup>18</sup> (molecular vibrations and a good general introduction to group theory), and Sponer and Teller<sup>19</sup> (electronic spectra of molecules). Original sources, many of which are due to Wigner and Weyl, are listed in the books quoted. We just mention Bethe<sup>20</sup> as a pioneer application of group theory to the splitting of energy levels in crystal fields, and Mulliken<sup>21</sup> where the first applications were suggested to the theory of molecular structure.

We shall now consider examples of the types of problems we propose to treat by group theory. It is well-known that, in one dimension, the inversion operation  $x \rightarrow -x$  permits us to classify functions in even and odd ones:

$$\begin{aligned} \text{even:} \quad & g(x) = g(-x), \\ \text{odd:} \quad & u(x) = -u(-x). \end{aligned} \tag{1}$$

The interest of this classification is due to the fact that it is *complete*, which means that any arbitrary function  $f(x)$  of one variable can always be expressed as a linear combination of even and odd functions.

$$f(x) = \frac{1}{2}[f(x) + f(-x)] + \frac{1}{2}[f(x) - f(-x)]. \tag{2}$$

The first and second square brackets in this expression are even and odd respectively under inversion. This result shows that, in one dimension, even and odd functions are the basic ones on which all others are built.

We shall extend these considerations to functions of more than one variable. The corresponding configuration spaces may now have symmetry operations other than inversion and we shall first aim at classifying functions in such spaces in symmetry types analogous to those given in one dimension by the relations (1). This will lead to the concept of *irreducible representation* (§ 1.7 and § 3.2). Secondly, in analogy with Eq. (2), we shall obtain expansions of arbitrary functions in terms of those of the various symmetry types permitted in any given configuration space (see § 5.3).

The next question is why such considerations are developed. Many useful results will appear in the course of this chapter, but here a simple example will indicate the advantage of using symmetry considerations. If we limit ourselves again to functions of one variable it is well known that a definite integral of the form

$$\int g(x)u(x) dx = 0 \tag{3}$$

vanishes whenever  $g(x)$  and  $u(x)$  are even and odd functions respectively. This is a most useful property, as matrix elements such as those that appear in perturbation problems are given by integrals similar to that in (3), so that the computations can be much simplified if simple cancellation properties, such as (3), are found for more general integrals. Equation (3) will therefore be extended for functions belonging to the various symmetry types of multidimensional spaces (see § 5.6).

To fulfill the programme just sketched we must first consider symmetry operations in some detail, which we do in § 1, where we shall not use any group theory but rather exploit the techniques for the representation of operators that are standard in quantum mechanics (see Vol. I, Chapter 1, § 4). We shall proceed as far as possible along these lines and we shall find then that some important questions remain unanswered within the framework of the elementary techniques. The existence of these difficulties suggests that it is necessary to develop a more elaborate technique. This is provided by group theory, the elements of which are given in § 2. This is then used in further sections so as to solve the various problems proposed in this introduction and in § 1.

## 1. Symmetry Operators and their Representation

### 1.1 What is a Symmetry Operation?

Suppose that we want to determine the energy of a state of the water molecule. There are in it two identical hydrogen atoms which, in order to write down the molecular Hamiltonian, must be labelled in some manner, as for instance in Fig. 1(a). The energy cannot change if the hydrogen atoms are labelled in a different manner, as in Fig. 1(b). In going from (a) to (b) we have effected a *covering operation* of the system which substitutes every particle by an identical one, that is, a *symmetry operation*. In our example, this is a reflection on the  $yz$  plane (see Fig. 1).

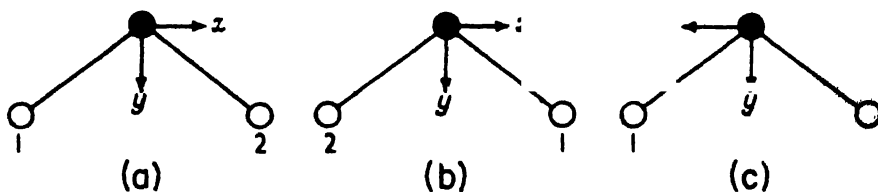


FIG. 1. Symmetry operations. The  $z$ -axis is perpendicular to the plane of the figure.

It is important to notice that, if our water molecule is in free space, its position can be changed in any manner without altering its energy. Hence, (c) and (b) on Fig. 1 are just identical arrangements. (In fact an observer sitting on the molecule in free space would not be able to discover any changes in going from (b) to (c).) This means that the change (a)  $\rightarrow$  (b) is the same as (a)  $\rightarrow$  (c), so that our symmetry operation is nothing more than

a change of axes. It should be carefully noted that we always consider in this chapter symmetry operations as changes of axes.

### 1.2 Degeneracy

The property of degeneracy of the energy levels of physical systems is normally associated with the existence of some particular symmetry. We shall now illustrate this point. In going from (a) to (c) in Fig. 1, the energy levels of the water molecule cannot change because the energy is a scalar quantity. On the other hand, vectorial quantities, like the momentum, do change under changes of axes, so that different eigenvalues and eigenfunctions will correspond to them in the different systems of axes. If a vectorial quantity commutes with the Hamiltonian (Vol. I, Chapter 2, § 3.3) these various eigenfunctions will also be eigenfunctions of the Hamiltonian which, because this latter is invariant under the symmetry operation effected, correspond to the same value of the energy. Hence the energy level is degenerate.

Consider as an example a free particle of mass  $m$  moving from left to right in one dimension with an eigenvalue  $k$  of the momentum operator  $p$ . Its energy is  $E = k^2/2m$ , and the corresponding momentum eigenfunction is  $\exp(2\pi i k x)$  (Vol. I, see Chapter 4, § 1.1). If we change the  $x$ -axis into  $-x$  the value of the momentum becomes  $-k$ , the energy is unchanged, and the new eigenfunction of  $p$  corresponding to the value  $-k$  is  $\exp(-2\pi i k x)$ . As  $p$  and  $H$  commute  $\exp(2\pi i k x)$  and  $\exp(-2\pi i k x)$  are eigenfunctions of the Hamiltonian, and they correspond to the single value of the energy  $E = k^2/2m$ . The origin of this degeneracy is the inversion symmetry of the free one-dimensional space on which the particle is moving.

The above considerations indicate that the study of symmetry and hence that of group theory will play an important part in the treatment of degeneracy. Actually, several different eigenfunctions may correspond to the same eigenvalue just by chance, rather than on account of a symmetry property. This type of degeneracy is called *accidental* (see § 3.4).

### 1.3 Symmetry Operations

We shall consider some general properties of symmetry operations. When we change the axes  $x, y, z$  into  $x', y', z'$ , the coordinates of a point  $q$  are changed into new coordinates  $q'$ . We can write  $q' \equiv Rq$ , where  $R$  is the *operator* that represents the change of axes in question. The above is in fact its definition. It is clear that these operators can be applied on vectors as well as on points.

Two symmetry operations,  $R$  and  $S$ , say, can always be compounded. We use the symbol  $RS$  for the composite operation in which first  $S$  and secondly  $R$  are effected. This symbol must then be read from right to left and it is clear that it also expresses a symmetry operation.

Given a symmetry operation  $R$  of a given system, there is always a symmetry operation of the same system which, applied before or after  $R$ , cancels it out, i.e., that leaves the system exactly as it was before  $R$  was applied. This operation is denoted with the symbol  $R^{-1}$  and is called the *reciprocal* of  $R$ . The definition given can be stated in symbols as follows:  $RR^{-1} = R^{-1}R = E$ , where  $E$  stands for the *identity* operation which leaves the system undisturbed.

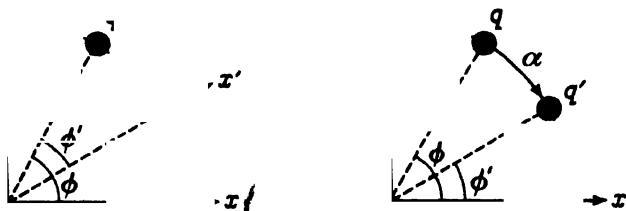


FIG. 2. Rotation of axes. The  $z$ -axis is perpendicular to the plane of the figure

The interpretation of symmetry operations as changes of axes is sometimes called the *passive interpretation*, and its meaning will be clarified in Fig. 2. When we rotate the  $x$ -axis by  $\alpha$  around the  $z$ -axis, the coordinates  $q$  of a given point go into the new coordinates  $q'$ . The point itself, of course, remains fixed. Although we shall always consider the symmetry operations in the passive interpretation, it is often easier to visualize them by imagining that the points themselves (or the corresponding vectors), rather than the axes, are moved. This is the *active interpretation* of the symmetry operations (Fig. 2 b). By comparing Fig. 2 (a) and (b) we see that if we want to move the original point  $q$ , so that its coordinates become  $q'$  we must rotate the point by the angle  $-\alpha$ . In general an operation  $R$  on the axes can be visualized as an operation  $R^{-1}$  acting on the points of the space. We shall often do this.

We shall now enumerate the more important symmetry operations. *Rotations* are operations that leave only a point, or at most an axis, invariant. We shall be concerned with finite rotations for which the rotation angle can always be expressed as  $2\pi/n$  ( $n$  integral). Then, the corresponding axis is an  $n$ -fold one (binary, ternary, etc.) and we shall denote such rotations



with the symbol  $C_n$ . *Positive rotations* are those which, on introducing a (right or left-handed) system of axes  $x, y, z$ , with  $z$  in the direction of the rotation axis, take the positive half of the  $x$  axis into the positive half of the  $y$  axis. *Negative rotations* are defined the other way round. The *inversion* operation  $i$  is the one that takes the axes  $x, y, z$  into  $-x, -y$ , and  $-z$  respectively. A *reflection* in a plane can always be described as the product of a binary rotation (rotation by  $\pi$ ) around an axis perpendicular to the plane and the inversion (see Fig. 3). Reflections are represented with the symbol  $\sigma$ . We see from the figure that  $\sigma = iC_2 = C_2i$ .

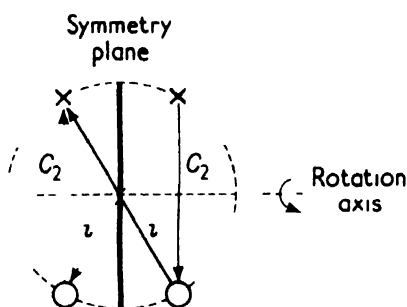


FIG. 3 Reflections  $\times$ , point above the plane of the drawing,  $\circ$ , point below the plane of the drawing. The arrows indicate that we use the active interpretation, which does not introduce any difference here because  $\sigma^{-1} = \sigma$ . The symmetry plane is perpendicular to the plane of the figure and the rotation axis lies in the latter.

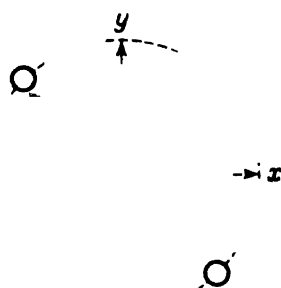


FIG. 4 An alternating axis ( $S_4$ )  $\times$ , point above the plane of the drawing;  $\circ$ , point below the plane of the drawing.  $S_4$ , perpendicular to the plane of the figure, coincides with the  $z$ -axis.

Other important symmetry operations are the *rotary reflections*. As an example, we represent in Fig. 4 the position of the four hydrogen atoms in the methane molecule  $\text{CH}_4$ , which occupy the corners of a regular tetrahedron. To go from one of the hydrogen atoms to an equivalent one we rotate by  $2\pi/4$  around the  $z$ -axis and reflect in the  $xy$  plane. In general, the rotary reflection  $S_n$  consists of a rotation by  $2\pi/n$  about an axis, followed (or preceded) by a reflection on a plane perpendicular to it. The corresponding axis is called an *alternating axis*.

Translations, glide reflections, and screw rotations are other symmetry operations which are important in crystals (see Burckhardt<sup>16</sup>).

Two symmetry operations may not commute, that is we may have  $RS \neq SR$ . As an example, let us consider the symmetry operations of

the system represented in Fig. 5. The only symmetry operations in such a system are the identity  $E$ , two threefold rotations  $C_3^+$  and  $C_3^-$ , and three reflections  $\sigma_1$ ,  $\sigma_2$ , and  $\sigma_3$ . We see from the figure that  $C_3^+ \sigma_2 = \sigma_3$  (remember that this means  $\sigma_2$  followed by  $C_3^+$ ) whereas  $\sigma_2 C_3^+ = \sigma_1$ . We shall find in § 1.4 a general rule about the commutability of symmetry operations.

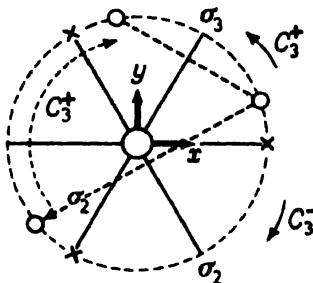


FIG. 5. The symmetry operations of the group  $C_{3v}$  (see Table XI, p. 159).  $\times$ , point below the plane of the drawing;  $\circ$ , point above the plane of the drawing. The latter is not a symmetry plane, neither are the full lines of the figure binary rotation axes. The small circles are not material points, (points that determine the symmetry of the system), but rather points in the space that are transformed under the symmetry operations of the system. Notice that the result of  $C_3^+$  is represented in the active interpretation, so that the point given is moved in the direction corresponding to  $C_3^-$ . This figure can be considered as a representation of the  $\text{NH}_3$  molecule, with the N atom at the position of the central circle, and the three H atoms at the positions of the crosses. (See Fig. 8.)

It will be useful to find the reciprocal of the product  $RS$  of two operations. By definition this must satisfy the relation  $(RS)(RS)^{-1} = E$  which is fulfilled by taking

$$(RS)^{-1} = S^{-1}R^{-1}, \quad (4)$$

because  $RSS^{-1}R^{-1} = RR^{-1} = E$ .

It is easy to see that the symmetry operators are *linear*. In fact, if  $\mathbf{u}$  and  $\mathbf{v}$  are any two vectors such that  $\mathbf{w} = \mathbf{u} + \mathbf{v}$  is their sum, it is clear that  $R\mathbf{w} = R(\mathbf{u} + \mathbf{v}) = R\mathbf{u} + R\mathbf{v}$ . (That is, the sum of the transformed vectors is equal to the transform of their sum.) It is also clear that if  $c$  is a constant  $Rc\mathbf{u} = cR\mathbf{u}$ . The two properties just illustrated are those that characterize linear operators.

## 1.4 Representatives of Operators

We shall now find an algebraic representation of general linear operators. The method which we shall follow could in principle be used to represent

the symmetry operators considered hitherto, but in practice these are always represented by the matrix of the transformation, defined in the conventional manner in terms of the coordinates rather than the unit vectors, as we shall do here. The definition which we shall give is in fact the same used to represent the quantal operators in terms of matrices (see Vol. I, Chapter 1, § 4) and will be useful to describe some more general symmetry operators to be defined in § 1.5.

Let us consider a complete set of orthogonal unit vectors  $\xi_r, r = 1, 2, \dots, n$ . The orthonormality condition requires that the scalar product of any two vectors be zero and that of a vector by itself (that is, the length of the vector) be unity:  $\xi_i \cdot \xi_j = \delta_{ij}$  ( $\delta_{ii} = 1, \delta_{ij} = 0$  when  $i \neq j$ ). In considering cases as general as possible where the vectors  $\xi$  can be complex, or identified with entities such as functions, we generalize the scalar product which we now represent with the symbol  $(\xi_i, \xi_j)$  as follows:  $(\xi_i, \xi_j) \equiv \int \xi_i^* \xi_j d\tau$ , where  $d\tau$  is the volume element of the configuration space in which  $\xi_i$  and  $\xi_j$ , considered now as functions, are defined. In this definition we take the complex conjugate of the first vector, so that  $(\xi_i, \xi_i)$ , which is the length of the vector  $\xi_i$ , be always real, as it must, even when  $\xi_i$  is complex. Given an operator  $S$ , we call  $S\xi_i$  the vector that results from operating with  $S$  on the unit vector  $\xi_i$ .<sup>\*</sup> As the  $\xi_r$  form a complete set the vector  $S\xi_i$  must be expressible as a linear combination of them:

$$S\xi_i = \sum \xi_r D(S)_{ri} \quad (5)$$

where the coefficients in the linear expansion are denoted with  $D(S)_{ri}$ . They are put to the right of the unit vectors rather than to their left, so as to satisfy a further requirement to be specified below.

Equation (5), applied for  $i = 1, 2, \dots, n$ , defines a matrix which we call the *representative* of the operator  $S$ . In fact, if we denote the row vector of components  $\xi_1, \xi_2, \dots, \xi_n$  with the symbol  $\langle \xi |$  we have

$$S \langle \xi | = \langle \xi | D(S). \quad (6)$$

The matrix  $D(S)$  varies if we define it with respect to a different set of unit vectors, and it should properly be denoted with  $D_\xi(S)$  to express this fact. However we shall use the full notation only when necessary (see § 1.6). The row vector  $\langle \xi |$  on which an operator is represented is called the *basis* of the representation. It should be noticed that the symbol  $S \langle \xi |$  in (6) means the row vector  $\langle S\xi |$ .

<sup>\*</sup>  $S\xi$  here must be read as just one symbol, like  $\xi'$ , say.

We must require from the matrix representatives that they satisfy a very important property, namely the *conservation of the multiplication rule*. This means that the representative of the product of two operators  $R$  and  $S$  must be given by the product of their representatives,

$$D(RS) = D(R)D(S). \quad (7)$$

In fact, we have for the operator  $R$ , just as in (5)

$$R\xi_r = \sum_s \xi_s D(R)_{sr}. \quad (8)$$

We now apply  $R$  on both sides of Eq. (5) and, on account of the linearity of the operator its right-hand side is expressed in terms of the vectors  $R\xi_r$ . These are given by Eq. (8), so that we have

$$RS\xi_i = \sum_s \xi_s \sum_r D(R)_{sr} D(S)_{ri} = \sum_s \xi_s [D(R)D(S)]_{si}, \quad (9)$$

where in the last step we use the standard definition of the matrix product. If we compare Eq. (9) with the definition of the representative  $D(RS)$  of the operator  $RS$ :  $RS\xi_i = \sum_s \xi_s D(RS)_{si}$ , we see that condition (7) is satisfied.\*

We can obtain a direct definition of the matrix elements  $D(S)_{ri}$  of the representatives by exploiting the orthonormality property of the unit vectors  $\xi_r$ :  $\int \xi_i^* \xi_j d\tau = \delta_{ij}$ . It is enough to multiply (5) by  $\xi_i^*$  and integrate over  $d\tau$ . Then,

$$D(S)_{ri} = \int \xi_i^* S\xi_r d\tau \equiv (\xi_i, S\xi_r). \quad (10)$$

The above treatment is quite general and it can be applied straight away to the symmetry operators previously considered. In fact, we shall now go back to the symmetry operators to show that they are *unitary*. This property is the mathematical expression of the following requirement, that must be satisfied by the symmetry operators: they must not stretch or deform in any manner the space on which they act. It is easy to put this condition into mathematical terms — we must require that the scalar product

\* The first part of Eq. (9) could have been written as  $RS\xi_i = R(S\xi_i) = \sum_r S\xi_r D(R)_{ri}$ . However, the matrix  $D(R)$  should now carry the label  $D_{S\xi}(R)$ , so that, to proceed with our proof, we would require an expression for  $D_{S\xi}(R)$  in terms of  $D_\xi(R)$  (see § 1.6, Eq. 23). In fact, in the proof given in the text all the matrices are defined in the same basis. In other, formally similar, cases of matrix operations the bases are left floating and a *modus operandi* as the one just suggested is used.

of two vectors (on which lengths and angles depend) be invariant with respect to the symmetry operators, i.e.

$$(\xi, \xi) = R(\xi, \xi) = (R\xi, R\xi).$$

If we now recall the definition of the *adjoint*  $R^\dagger$  of an operator  $R$  (see Vol. I, Chapter 1, § 3.2) as the operator that satisfies the condition  $(R^\dagger \xi, \xi) = (\xi, R\xi)$ , we have  $(R\xi, R\xi) = (R^\dagger R\xi, \xi)$ . Therefore,  $(\xi, \xi) = (R^\dagger R\xi, \xi)$ , which requires that  $R^\dagger R = E$ . This is the condition that defines the unitary operators.

It will be useful to find a relation between the matrix representative  $D(R^\dagger)$  of the adjoint of an operator and that of the operator itself. We shall find  $D(R^\dagger) = D(R)^\dagger$ , where the dagger, applied to a matrix, denotes the conjugate of its transpose, also called the *adjoint matrix*:  $D(R) \equiv \overline{D(R)}^*$ . (Remember that  $\overline{D(R)}_{ij} = D(R)_{ji}$ , defines the transpose of a matrix, that is, the matrix in which the rows and columns of the original one have been interchanged). In fact, from (10),

$$D(R^\dagger)_{ij} = (\xi_i, R^\dagger \xi_j) = (R\xi_i, \xi_j).$$

(The last step results from the definition of the adjoint of an operator). Now

$$(R\xi_i, \xi_j) = (\xi_i, R\xi_j)^* = D(R)_{ji}^* = \overline{D(R)}_{ij}^* \equiv D(R)^\dagger_{ij}.$$

The meaning of the result just obtained is simple — the representative of the adjoint of an operator is the adjoint of the matrix representative of the same operator.

It is often advantageous to reason in terms of the matrix representatives of the operators rather than of the operators themselves. As an example, let us consider the commutation properties of operators. If two operators commute, so must their matrix representatives, because of the conservation of the multiplication rule. The necessary and sufficient condition for two matrices to commute is that they have the same eigenvectors.

Consider for instance a binary rotation around the  $z$ -axis,  $C_{2z}$ . To find its eigenvectors we notice that the unit vector in the  $z$  direction,  $\mathbf{z}$ , is left invariant by  $C_{2z}$ , that is, it is an eigenvector corresponding to the eigenvalue  $+1$ . All the unit vectors in the  $xy$  plane perpendicular to the  $z$ -axis, are changed in sign by  $C_{2z}$  so that they all correspond to the eigenvalue  $-1$ . They form clearly a degenerate set, the degree of degeneracy of which is equal to 2, as we can find two independent unit vectors,  $\mathbf{x}$ , and  $\mathbf{y}$ , on which all others can be expressed. Summarizing, the eigenvectors are  $\mathbf{z}(1)$ ,  $\mathbf{x}(-1)$ , and  $\mathbf{y}(-1)$ , where we give the corresponding eigenvalues in

brackets. Analogously, we find that the eigenvectors and eigenvalues of a rotation around  $x$ ,  $C_{2x}$  are  $x(1)$ ,  $y(-1)$ , and  $z(-1)$ . Therefore  $C_{2x}$  and  $C_{2y}$  commute. In general, we can see from the above argument that any two binary rotations around perpendicular axes commute.

The inversion operation  $i$  commutes with all operations, since its eigenvectors, as those of the identity, are all the vectors of the space (whereas the corresponding eigenvalues are all equal to  $-1$ ).

As we know, reflections are products of the inversion by binary rotations around axes perpendicular to the reflection planes. Hence, two reflections will commute if and only if their reflection planes are perpendicular.

### 1.5 Symmetry Operators in the Function Space

Consider a symmetry operation  $R$  in a configuration space, so that the coordinates  $q$  of a point before the transformation take the value  $q' = Rq$  after it. Suppose now that we have defined a function in the configuration space considered (e.g., a temperature field in it). This function can be represented with the symbol  $f(q)$  in the original set of coordinates. When this is transformed under an operation  $R$  it must be clearly understood that the values of the function at each point of the space are left unaltered. (This is so because the transformations are changes of axes only, that do not drag the space with them and neither therefore functions defined in it.) The functional relation represented by  $f$  with respect to the coordinates  $q$  will however be changed to, say,  $f'$  with respect to the coordinates  $q'$ . (See the example below.) We can say that the transformation  $R$  in the configuration space *induces* a transformation in the function space. We represent this induced operator in the function space with the symbol  $R$ . In the same manner that the relation  $q' = Rq$  can be taken as the definition of the configuration space operator  $R$ , the relation  $f' = Rf$  is the definition of the operator  $R$ .

As the quantity that defines the function at every point is left unaltered by the transformation, we have the relation

$$f(q) = f'(q'), \quad (11)$$

that is

$$f(q) = Rf(Rq). \quad (12)$$

On applying this relation to the point of coordinates  $R^{-1}q$ , we obtain

$$Rf(q) = f(R^{-1}q). \quad (13)$$

This expression can be taken as our fundamental rule to relate a transformation in the function space to its parent transformation in the configuration

space. It can be stated as follows: the value of the function  $Rf$  at the point  $q$  is equal to the value of the function  $f$  at the point  $R^{-1}q$ .\*

The above considerations are of crucial importance in the study of the symmetry properties of functions, as these are defined with relation to the function space operators just introduced. As an example of the use of Eq. (13) let us consider the well-known functions

$$p_x = \sin \theta \cos \phi, \quad (14)$$

$$p_y = \sin \theta \sin \phi, \quad (15)$$

which are the angular part of the solutions of the Schrödinger equation for a central field system.<sup>†</sup> We represent the function  $p_x$  in Fig. 6 (a).

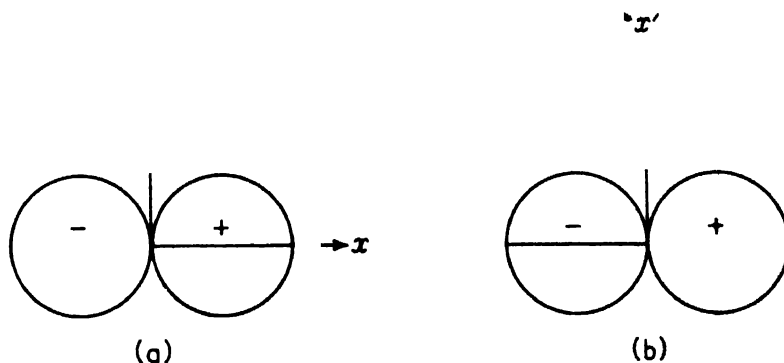


FIG. 6 Transformation of  $p_x$  (a) under a rotation by  $\pi/2$

It is clear that when we rotate the axes counterclockwise by  $\pi/2$  (Fig. 6 b) the function  $p_x$  goes into  $-p_y$ . (The function  $p_y$  of course, has its positive lobe in the positive branch of the  $y$ -axis.) If we represent with  $C_{\pi/2}$  the rotation of axes effected, we can write the corresponding function transformation as follows,  $C_{\pi/2}p_x = -p_y$ . We can also obtain this result by using the expression (13),  $C_{\pi/2}p_x = \sin \theta \cos (C_{\pi/2}^{-1}\phi)$ . The clockwise rotation  $C_{\pi/2}^{-1}$  changes  $\phi$  into  $\phi + \pi/2$ , so that  $C_{\pi/2}p_x = -\sin \theta \sin \phi = -p_y$ , just as before.

\* It is important to remember that  $Rf$  should be read as one symbol, just in the same manner as  $f'$  say, is understood as a single symbol. Accordingly  $R/g$ , read just as  $(/g)'$ , is the transform of  $/g$  under  $R$ , that is  $R/g = R/Rg$ .

<sup>†</sup> It should be noticed that these functions are just spherical harmonics in real form,  $p_x = (Y_1^1 + Y_1^{-1})/\sqrt{2}$ ,  $p_y = -i(Y_1^1 - Y_1^{-1})/\sqrt{2}$ , so that the example considered in the text will also serve as an introduction to the fact (§ 6.5) that the spherical harmonics form bases for the representations of rotations.

A very important property of the operators in the function space is that they maintain the multiplication rule for the corresponding configuration space operators. That is, if

$$RS = T, \quad (16)$$

then,

$$RS \equiv T, \quad (17)$$

where in every case a sans serif operator is related to the corresponding italic one by Eq. (13). To prove this result let us consider the function  $RSf(q) \equiv R[Sf(q)]$ , because the operators must be applied from right to left. The last symbol, by (13), is the value of the function  $Sf$  at the point  $R^{-1}q$ . Therefore  $RSf(q) = Sf(R^{-1}q)$ . On applying (13) again to the right-hand side of this expression, we have

$$RSf(q) = f(S^{-1}R^{-1}q) = f(T^{-1}q) = Tf(q)$$

which verifies (17).

## 1.6 Representation of the Function Space Operators

The method described in § 1.4 can be readily used to obtain representatives of the function space operators. It is enough to take as the unit "vectors" of the basis, functions  $\varphi_i$  that form a complete orthonormal set,<sup>†</sup> so that  $\int \varphi_i^* \varphi_j d\tau = \delta_{ij}$ . Then, Eq. (5) and (10) of § 1.4 take respectively the form

$$R\varphi_j = \sum \varphi_i D(R)_{ij}, \quad (18)$$

$$D(R)_{ij} = \int \varphi_i^* R\varphi_j d\tau \equiv (\varphi_i, R\varphi_j). \quad (19)$$

As an example, let us find a representative for the operator  $C_\alpha$ , which corresponds to a rotation by  $\alpha$  around an axis  $z$ , say. We shall use for our basis the functions  $p_x, p_y$  defined in § 1.5. Just as in the last section we have

$$C_\alpha p_x = \sin \theta \cos (C_\alpha^{-1} \phi) = \sin \theta \cos (\phi + \alpha) = p_x \cos \alpha - p_y \sin \alpha.$$

Analogously,

$$C_\alpha p_y = p_x \sin \alpha + p_y \cos \alpha.$$

<sup>†</sup> A prescription will be given in § 3.3 and § 5 to obtain sets of functions suitable as a basis.



These two equations can be written in matrix form

$$C_\alpha \langle p_x, p_y | = \langle p_x, p_y | \begin{vmatrix} \cos \alpha & \sin \alpha \\ -\sin \alpha & \cos \alpha \end{vmatrix} \quad (20)$$

so that (cf. 6),

$$D(C_\alpha) = \begin{vmatrix} \cos \alpha & \sin \alpha \\ -\sin \alpha & \cos \alpha \end{vmatrix}. \quad (21)$$

As a further example we shall obtain the representative on the basis  $\langle p_x, p_y |$  of a reflection  $\sigma$  on a plane. Let  $\Phi$  be the azimuth of the mirror plane and  $\phi$  that of a point, which is transformed under the reflection into  $\phi' \equiv \sigma\phi$ , as shown in Fig 7

It is clear from the figure that

$$\begin{aligned} \phi' &\equiv \sigma\phi \\ &= \phi + 2(\Phi - \phi) = 2\Phi - \phi \end{aligned}$$

Hence,

$$\begin{aligned} \sigma p_x &= \sin \theta \cos (\sigma^{-1}\phi) \\ &= \sin \theta \cos (\sigma\phi) \\ &= \sin \theta \cos (2\Phi - \phi) \\ &= p_x \cos 2\Phi + p_y \sin 2\Phi. \end{aligned}$$

Analogously,

$$\sigma p_y = p_x \sin 2\Phi - p_y \cos 2\Phi$$

so that

$$D(\sigma) = \begin{vmatrix} \cos 2\Phi & \sin 2\Phi \\ \sin 2\Phi & -\cos 2\Phi \end{vmatrix} \quad (22)$$

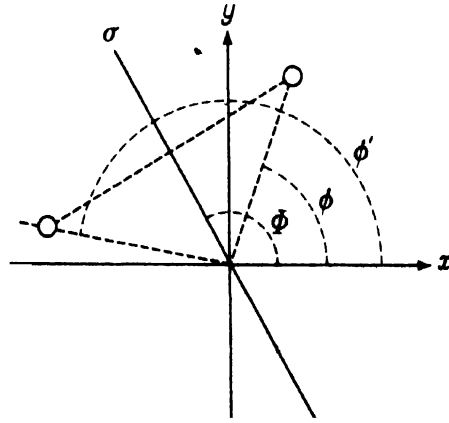


FIG 7 Transformation of the azimuth of a point under a reflection.

We shall now show that the matrix representatives of the function space operators are unitary. That the operators themselves are unitary is obvious, from the unitary property of the configuration space operators ( $R^\dagger R = E$ ), and the conservation of the multiplication rule, so that  $R^\dagger R = E$ . From this relation we have  $D(R^\dagger)D(R) = D(E) = 1$ , where 1 is the unit matrix. Now, as shown in § 15,  $D(R^\dagger) = D(R)^\dagger$ , so that  $D(R)^\dagger D(R) = 1$  and  $D(R)$  is unitary.

Exactly as in § 1.4 we say that the functions  $\varphi_i$  form a basis for the representation of the operator  $R$  or also that they *span a representation*

space of  $R$ . In this latter case we use a geometrical language in which the functions of the basis are identified with the unit vectors in terms of which all the vectors of a space can be given.

Also as before, the matrices  $D(R)$  depend on the basis used and a complete notation for them should properly include a label for the basis used, as in  $D_\varphi(R)$ . We shall presently use this complete notation as we want to find how the representative  $D_\varphi(R)$  is transformed when we change the basis  $\langle \varphi |$  into another one  $\langle \psi |$ . Let us suppose that the functions of this new basis are derived from those of the old one by a transformation with an operator  $U$ ,  $\psi = U\varphi$ . Now, from (19),

$$D_\psi(R)_{ij} = (\psi_i, R\psi_j) = (U\varphi_i, RU\varphi_j) = (\varphi_i, U^\dagger RU\varphi_j) = D_\varphi(U^\dagger RU)_{ij}.$$

Therefore,

$$D_\psi(R) = D_\varphi(U^\dagger RU) = D_\varphi(U)^\dagger D_\varphi(R) D_\varphi(U),$$

where we use the fact that  $D_\varphi(U^\dagger) = D_\varphi(U)^\dagger$ . If  $U$  is also unitary, this expression can be written as follows:

$$D_\psi(R) = D_{U\varphi}(R) = D_\varphi(U)^{-1} D_\varphi(R) D_\varphi(U) \quad (23)$$

and this is called a *similarity transformation*, or a *unitary transformation* in matrix theory. It possesses the important property of preserving the original multiplication rule for the matrices  $D_\varphi(R)$ . In fact, if  $D_\varphi(R)D_\varphi(S) = D_\varphi(T)$ , then,

$$\begin{aligned} D_\psi(R) D_\psi(S) &= D_\varphi(U)^{-1} D_\varphi(R) D_\varphi(U) D_\varphi(U)^{-1} D_\varphi(S) D_\varphi(U) \\ &= D_\varphi(U)^{-1} D_\varphi(T) D_\varphi(U) = D_\psi(T). \end{aligned}$$

If we have two different, independent bases,  $\langle \lambda_1, \dots, \lambda_l |$ ,  $\langle \mu_1, \dots, \mu_m |$  we can form a third one by constructing the vector  $\langle \nu | \equiv \langle \lambda_1, \dots, \lambda_l, \mu_1, \dots, \mu_m |$ . This vector is called the *direct sum* of the two vectors given. It is clear that the representative  $D_\nu(R)$  on this basis will have the form:

$$D_\nu(R) = \begin{array}{c} D_\lambda(R) \\ -l \rightarrow D_\mu(R) \\ \leftarrow m \end{array}$$

In fact, a transform such as  $R\lambda_i$  must be given as

$$R\lambda_i = \sum_{r=1}^{l+m} \lambda_r D_\nu(R)_{ri} = \sum_{r=1}^l \lambda_r D_\lambda(R)_{ri}.$$

Hence,  $D_\nu(R)_{ri} = D_\lambda(R)_{ri}$  for  $r \leq l$  and  $D_\nu(R)_{ri} = 0$  for  $r > l$ .

The matrix  $D_\nu(R)$  is called the *direct sum* of the matrices  $D_\lambda(R)$  and  $D_\mu(R)$ .

The above considerations can clearly be extended to any number of bases. The corresponding representatives, or *direct sum matrices*, will be given as an array of matrices stuck along the diagonal. Such matrices will be called *block-diagonal matrices*.\*

If we obtain a representative that is a block-diagonal matrix, it is clear that its basis separates out in two (or more) independent sub-bases and that each of the blocks of the representative is itself a representative.

### 1.7 An Example: Introduction to the Reduction of Representations

Let us consider the arrangement of particles shown in Fig. 8, which has exactly the same symmetry operations as that of Fig. 5, that is,  $E, C_3^+, C_3^-, \sigma_1, \sigma_2, \sigma_3$ .

To fix our ideas we can think of the figure as a representation of the ammonia molecule, the open circle being the N atom and the black ones the H atoms. To simplify our example we assume that the "N-H bonds" 1,2,3, form right angles one with the other so that, as the nitrogen ground state configuration is  $1s^2 2s^2 2p_x 2p_y 2p_z$ , we can suppose that the three  $2p$  orbitals lie in the orthogonal directions 1,2,3, shown in the figure. For convenience, we

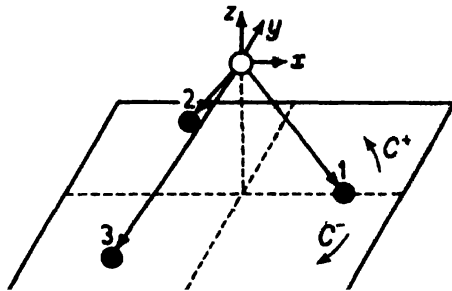


FIG. 8. A perspective of the system represented in Fig. 5.

shall designate them with the symbols  $p_1, p_2$  and  $p_3$ , and we shall first use them as a basis on which to obtain representatives for all the symmetry operations of the system. To do this, we first require a transformation table (Table I) where the functions  $Rp_i (i = 1, 2, 3)$  are given for all the operations  $R$  considered. The corresponding values of  $i$  are listed in the table in the intersection of the row corresponding to  $R$  with the column corresponding to  $p_i$ .

\* More properly, it is convenient to define a *supermatrix* as a matrix, the elements of which are themselves matrices. Hence a block-diagonal matrix is just a *diagonal supermatrix*. It can be readily seen that the matrix multiplication rule is valid for supermatrices.

TABLE I  
TRANSFORMATION PROPERTIES OF THE FUNCTIONS  $p_1$ ,  $p_2$  AND  $p_3$

	$p_1$	$p_2$	$p_3$
E	1	2	3
$\sigma_1$	1	3	2
$\sigma_2$	3	2	1
$\sigma_3$	2	1	3
$C^+$	3	1	2
$C^-$	2	3	1

In obtaining the table the following simple rule may be found useful. The transform  $Rf$  of a function  $f$  is the function that comes instead of  $f$  if the operation  $R$  is thought of as dragging the functions with it. It is also useful to note that Table I can be employed to obtain the multiplication rules of the operators, as an alternative to the graphical method of § 1.3. For instance,

$$C^+ \sigma_2 \langle 123 | = C^+ \langle 321 | \stackrel{!}{=} \langle 213 | = \sigma_3 \langle 123 | \quad (24)$$

so that  $C^+ \sigma_2 = \sigma_3$ , in agreement with the result of § 1.3

We shall now obtain the representatives of the operators considered. We can use Eq. (19) for this purpose. For instance,

$$D(\sigma_1)_{11} = \int p_1^* \sigma_1 p_1 d\tau = \int p_1^* p_1 d\tau = 1,$$

$$D(\sigma_1)_{12} = \int p_1^* \sigma_1 p_2 d\tau = \int p_1^* p_3 d\tau = 0,$$

and so on. (We use here the results of Table I and the fact that  $\int p_i p_j d\tau = \delta_{ij}$ .) We then obtain

$$D(\sigma_1) =$$

Often a more direct method is quicker. We can write:

$$1$$

$$\sigma_1 \langle 123 | = \langle 132 | = \langle 123 |$$

## 2. GROUP THEORY

The matrix here, which is the representative sought (see Eq. 6) is found by inspection on using the condition that its product with the vector of the basis must give the transform of the latter ( $\langle 132|$  in the case above).

We can obtain by either method all the representatives required and they are listed in Table II.

TABLE II  
REPRESENTATIVES IN THE BASIS  $\langle p_1 p_2 p_3 |$

E	$\sigma_1$	$\sigma_2$	$\sigma_3$	$C_3^+$	$C_3^-$
$\begin{vmatrix} 1 & & \\ & 1 & \\ & & 1 \end{vmatrix}$	$\begin{vmatrix} 1 & & \\ & 1 & \\ & & 1 \end{vmatrix}$	$\begin{vmatrix} & 1 & \\ & & 1 \\ 1 & & \end{vmatrix}$	$\begin{vmatrix} & 1 & \\ 1 & & \\ & & 1 \end{vmatrix}$	$\begin{vmatrix} & 1 & \\ & & 1 \\ 1 & & \end{vmatrix}$	$\begin{vmatrix} & & 1 \\ 1 & & \\ & 1 & \end{vmatrix}$

It is now easy to verify that the multiplication rule for the operators is preserved by their representatives. For instance,

$$D(C^+) D(\sigma_2) = \begin{vmatrix} & 1 & \\ & & 1 \\ 1 & & \end{vmatrix} \begin{vmatrix} & 1 & \\ & & 1 \\ 1 & & \end{vmatrix} = \begin{vmatrix} & 1 & \\ 1 & & \\ & & 1 \end{vmatrix} = D(\sigma_3).$$

For convenience, we shall use a terminology that will be fully explained later on (§ 3.1) and shall refer to the set of matrices obtained as a *representation* of the set of operators considered. Let us now find a second representation, by using as the basis the functions  $\langle p_x p_x p_y |$  directed along the corresponding axes shown in Fig. 8. We first notice that  $p_x$  is left invariant by all the operations of the set. Hence,  $p_x$  on one side and  $p_x p_y$  on the other, do not "mix" under any operation, so that all the matrix representatives must have the form:

$$\begin{vmatrix} 1 & & \\ & a & b \\ & c & d \end{vmatrix}$$

We can obtain the  $2 \times 2$  part of these matrices by using the matrix (21) for the rotations  $C_3^+$  and  $C_3^-$  and the matrix (22) for the reflections  $\sigma_1$ ,  $\sigma_2$  and  $\sigma_3$ . The corresponding matrices are listed in the Table III.

TABLE III  
REPRESENTATIVES IN THE BASIS  $\langle p_x p_y |$

E	$\sigma_1$	$\sigma_2$	$\sigma_3$	$C_3^+$	$C_3^-$
$\begin{vmatrix} 1 & & \\ & 1 & \\ & & 1 \end{vmatrix}$	$\begin{vmatrix} 1 & & \\ & 1 & \\ & & -1 \end{vmatrix}$	$\begin{vmatrix} 1 & & \\ & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{vmatrix}$	$\begin{vmatrix} 1 & & \\ & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{vmatrix}$	$\begin{vmatrix} 1 & & \\ & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{vmatrix}$	$\begin{vmatrix} 1 & & \\ & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{vmatrix}$

It can be easily verified again that  $D(C_3^+)D(\sigma_2) = D(\sigma_3)$ .

We shall now consider again the meaning of the special structure shown by the matrices of Table III. They all have the same block-diagonal form (that is, they are  $2 \times 2$  diagonal matrices which have a  $1 \times 1$  and  $2 \times 2$  matrix as their diagonal elements). This is just an expression of the fact that the original basis  $\langle p_x p_y |$  separates out in two parts, each of which transforms independently under all the operations considered. These parts are themselves new bases  $\langle p_x |$  and  $\langle p_x p_y |$ , which each span a representation as shown in Table IV.

TABLE IV  
REPRESENTATIVES IN THE BASES  $\langle p_x |$  AND  $\langle p_x p_y |$

Basis	E	$\sigma_1$	$\sigma_2$	$\sigma_3$	$C_3^+$	$C_3^-$
$\langle p_x  $	1	1	1	1	1	1
$\langle p_x p_y  $	$\begin{vmatrix} 1 & \\ & 1 \end{vmatrix}$	$\begin{vmatrix} 1 & \\ & -1 \end{vmatrix}$	$\begin{vmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{vmatrix}$	$\begin{vmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{vmatrix}$	$\begin{vmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{vmatrix}$	$\begin{vmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{vmatrix}$

We can now summarize the steps in which the above result could have been obtained. We first use the basis  $\langle p_1 p_2 p_3 |$  and obtain the representation given in Table II. We now rotate the bases, under a transformation  $U$  that takes it to a new one  $\langle p_x p_y p_z |$ . ( $U$  is the rotation that takes the arrows 1,2,3 in Fig. 8 into the axes  $z, x, y$ , respectively. Its actual form will be given in § 3.5). The matrices of Table II therefore undertake a unitary trans-

formation (see Eq. 23) which takes them into those listed in Table III. These new matrices turn out to have all the same block-diagonal form, which means that their basis separates out, or has been reduced, into two (or more) parts. We shall therefore say that we have accomplished the *reduction* of the representation of Table II.

Let us now see what we have gained through the process of reduction. The matrix representatives give the symmetry behaviour of the functions of the basis. In some cases this symmetry behaviour can be considered as a typical one, in the sense that no other functions can be derived from those considered that behave in a simpler manner. For instance an arbitrary function in one dimension will not in general have a typical behaviour, as it can be transformed (Eq. 2) into even and odd functions that transform in a simpler manner. In the same way, we can say that the symmetry behaviour of the functions  $p_1, p_2, p_3$ , cannot be a typical one for a configuration space with the symmetry shown in Fig. 8, because they can be transformed into functions that transform in a simpler manner. In particular,  $p_z$  is invariant under all the possible operations, very much like the even functions in a one-dimensional space. However,  $p_x, p_y$  transform in a rather more complicated manner than we met in one dimension, and we are therefore faced with the following question. Is it possible to transform  $p_x, p_y$  into functions such that the two-dimensional matrices of Table IV can be further reduced? If this were the case, we would say that the new functions, rather than  $p_x, p_y$ , offer a typical symmetry behaviour.

We can now see fairly clearly which are the necessary steps for the classification of functions in symmetry types, as discussed in the introduction to this chapter. We must obtain representations for the set of all possible operations of the system, and reduce them repeatedly until further reduction is impossible. The functions that span the representations thus obtained, which are called *irreducible representations*, correspond to the various symmetry types of the system.

The example just considered shows that we can go quite a long way in this process by the methods given in this section. However, it also shows that two fundamental problems remain unsolved: First, how to recognize when a representation, like the two-dimensional one in Table IV, cannot be further reduced. Secondly, assuming this problem solved, i.e., for instance that we already know that the two representations of Table IV are irreducible, how to make sure that the symmetry types thus obtained are all those that are possible. (We could expect for instance, the existence of functions that do not transform under either of the two sets of matrices listed in Table IV.)

These two problems are clearly crucial in the theory of symmetry, and to solve them we shall have to make use of the techniques offered by group theory, the elements of which are discussed in the next section.

## 2. Elements of Group Theory

In order to answer the questions proposed at the end of the last section we must investigate in more detail the structure of the set of operations considered. This structure is given by the interrelations between the operators of the set, which were not considered at all in the last section, so that we may expect its analysis to lead to some progress in the right direction. To make the treatment of this section as general as possible the operators introduced in § 1 will be used only as examples.

### 2.1 Group Properties

If we examine the way in which the operators considered in the example of § 1.7 (listed in Table I) are interrelated, we shall soon discover that the essential characteristics of their relationships are expressed by the following properties, which we shall now list for any set  $\mathbb{G}$  of  $h$  entities  $G_1, G_2, \dots, G_h$ .

(1) There is a law of composition (called in general *multiplication*) between any two entities of the set, such that the result is always an element of the set.

$$G_i G_j = G_k, \quad G_k \in \mathbb{G}.$$

(2) This law of composition is associative.

$$G_i (G_j G_k) = (G_i G_j) G_k.$$

(3) There is an element of  $\mathbb{G}$ , say  $G_e$ , such that  $G_e G_i = G_i G_e = G_i$  for all  $i$ . This element will always be denoted with the symbol  $E$ , and is called the *identity element*.

(4) To each element  $G_i$  of  $\mathbb{G}$  there corresponds another element, say  $G_\mu$ , such that  $G_\mu G_i = G_i G_\mu = E$ . This element is called the *inverse* of  $G_i$  and is denoted with the symbol  $G_i^{-1}$ .

A set that possesses all these properties is called a *group*. To give an example of a group whose elements are not operators, it is easy to show that the set of all integral numbers forms a group when the law of composition considered is the addition. On the other hand, this is no longer the case when the law of composition is the multiplication, as the product by zero has no inverse.



The group properties that we have discussed ensure that, when the elements of a group are operators, they establish a one-to-one correspondence between their operands (that is, the entities on which they apply) and the results of the operations. This means that if  $R_i\alpha = \beta$ , this latter cannot be obtained by acting with  $R_i$  on a different operand  $\alpha'$ . In fact, if this were the case  $R_i\alpha = R_i\alpha'$  so that  $R_i$  could not have an inverse because then we would have  $R_i^{-1}R_i\alpha = \alpha'$ , and as  $\alpha \neq \alpha'$ ,  $R_i^{-1}R_i \neq E$ . Projections, for instance, are not one-to-one operations and hence have no inverse and cannot be group operations.

The structure of a group is completely given by means of its *multiplication table*, where the products of any two elements of the group are given. As an example, we give in Table V the multiplication table of the group of operators of the exercise of § 17, which, in a nomenclature to be explained in § 6.2, is denoted with the symbol  $C_{3v}$ . It should be noticed that in giving such a table it is necessary to specify the order in which the factors must be taken as, for instance, we do in the heading of Table V.

TABLE V  
MULTIPLICATION TABLE OF THE GROUP  $C_{3v}$ <sup>a</sup>

	$E$	$C_3^+$	$C_3^-$	$\sigma_1$	$\sigma_2$	$\sigma_3$
$E$	$E$	$C_3^+$	$C_3^-$	$\sigma_1$	$\sigma_2$	$\sigma_3$
$C_3^+$	$C_3^+$	$C_3^-$	$E$	$\sigma_2$	$\sigma_3$	$\sigma_1$
$C_3^-$	$C_3^-$	$E$	$C_3^+$	$\sigma_3$	$\sigma_1$	$\sigma_2$
$\sigma_1$	$\sigma_1$	$\sigma_3$	$\sigma_2$	$E$	$C_3^-$	$C_3^+$
$\sigma_2$	$\sigma_2$	$\sigma_1$	$\sigma_3$	$C_3^+$	$E$	$C_3^-$
$\sigma_3$	$\sigma_3$	$\sigma_2$	$\sigma_1$	$C_3^-$	$C_3^+$	$E$

<sup>a</sup> The element  $R_k = R_i R_j$  stands in the intersection of the row headed by  $R_i$  and the column headed by  $R_j$ .

It will be seen in the course of this chapter that all the information that we require about a group can be obtained from its multiplication table, without any reference to the nature of the elements of the group. We had to consider the latter in obtaining the products of the group elements. On the other hand, we could imagine the elements  $E, C_3^+, C_3^-, \sigma_1, \sigma_2$ , and  $\sigma_3$  given to us purely as symbols without any concrete meaning and their multiplication properties defined arbitrarily (but consistently) through

the multiplication Table V. This is possible because the multiplication table embodies all the group properties. A group defined in this way is called an *abstract group*.

## 2.2 Some Definitions and Theorems

An *Abelian* group is one for which any two elements commute, that is,  $G_i G_j = G_j G_i$  for all  $G_i, G_j$  in  $G$ .

The *order* of a group is the number of its elements. It can be finite or infinite.

A *complex* is any set of elements of a group. Complexes, as well as the groups themselves, are often represented with a notation due to Galois:  $H = H_1 + H_2 + \dots$ , where, of course, the addition sign is not used in the normal manner but just to indicate a juxtaposition of elements.

A *subgroup* is a complex of elements of a group which is in itself a group. The necessary and sufficient condition for a complex to be a subgroup is that the product of any two elements of the complex belongs to it. Example:  $E + C_3^+ + C_3^-$  in  $C_{3v}$  is a subgroup (see the multiplication table of  $C_{3v}$ , Table V).

A *right co-set* is a complex formed by multiplying on the right all the elements of a subgroup  $H$  of  $G$  by an element of  $G$ . Analogously we define a *left co-set*. A right co-set, say, is represented with the symbol:  $HG_i = H_1 G_i + H_2 G_i + \dots$

**Theorem 1.** If  $G_i \in H$  the right co-set  $HG_i$  is identical with  $H$  except at most for the order in which the elements are given.

*Proof.* All the elements of  $HG_i$  belong to  $H$  and their number is just the same as the order of  $H$ . Also, no two of them can be equal. For if  $H_k G_i = H_j G_i$ , then  $H_k^{-1} H_j G_i = G_i$ , so that  $H_k^{-1} H_j = E$ , and hence  $H_k = H_j$ . Therefore  $HG_i$  must contain all the elements of  $H$ .

**Theorem 2.** The right (or left) co-sets  $HG_i, HG_j$  of a subgroup are either identical or have no element in common.

*Proof.* Assume that they have one element in common.

$$H_i G_i = H_j G_j.$$

Then

$$H_i^{-1} H_j G_i = G_j.$$

Therefore

$$HG_j = HH_i^{-1} H_i G_i = HG_i.$$

In the last step we use the fact that  $H_i^{-1}H_i$  belongs to  $\mathbf{H}$  and that theorem 1 can therefore be applied.

**Theorem 3.** The order  $h'$  of a subgroup  $\mathbf{H}$  is a divisor of the order  $h$  of the group.

*Proof.* Let us form all the  $l$  different co-sets of  $\mathbf{H}$  (see theorem 2), say  $\mathbf{H}G_1, \mathbf{H}G_2, \dots, \mathbf{H}G_l$ . They contain  $h'l$  different elements and every element of the group appears once and only once in them. Hence  $h'l = h$ , which proves the theorem.

The quotient  $l = h/h'$ , which is the number of times that the order of a subgroup is contained in the order of the group is called the *index* of the subgroup.

Given an element  $G_i$  belonging to a group  $\mathbf{G}$  of finite order, the sequence  $G_i, G_i^2, G_i^3, \dots$  is a sequence of elements of  $\mathbf{G}$  and must be finite. For this to be the case we must have, for a certain  $n$ ,  $G_i^n = E$  which means that the elements  $G_i, G_i^2, \dots, G_i^n$  repeat themselves periodically. The set  $G_i, G_i^2, \dots, G_i^n \equiv E$  forms a subgroup and is called the *period* of the element  $G_i$ .  $n$  is defined as the *order* of the given element. (Note that the *order of an element* must not be confused with the order of a group.) As the order of an element is the order of the subgroup given by its period, it is (theorem 3) a divisor of the order of the group. As an example, in the group  $C_{3v}$  the period of  $C_3^+$  is  $C_3^+$ ,  $(C_3^+)^2 = C_3^-$ ,  $(C_3^+)^3 = E$ . That of  $\sigma_1$  is  $\sigma_1$ ,  $\sigma_1^2 = E$ .

A group that consists of just one period is called *cyclic*. As all the elements of a cyclic group can be given as powers  $G_i^s$  of the generating element  $G_i$ , the group is abelian:  $G_i^s G_i^t = G_i^{s+t} = G_i^t G_i^s$ . Any group of prime order must be cyclic, as the order of any element of it must be equal to the order of the group, so that the group is just made up of the period of one element.

The *product of two complexes*  $\mathbf{H} = H_1 + H_2 + \dots + H_n$  and  $\mathbf{J} = J_1 + J_2 + \dots + J_m$  can be defined in two different ways. The most direct definition is

$$\mathbf{HJ} = H_1J_1 + H_1J_2 + \dots + H_1J_m + \dots + H_nJ_1 + H_nJ_2 + \dots + H_nJ_m.$$

This, however, is seldom used, and we shall call it the *exceptional* definition of the product of complexes. The *standard* one consists in taking in the right-hand side of the above expression each element once and only once. As an example, consider a group  $\mathbf{G}$  of order  $h$ .  $\mathbf{GG}$  is equal to  $h\mathbf{G}$  in the exceptional definition (see theorem 1) and to  $\mathbf{G}$  in the standard one.

Given two groups  $\mathbf{G} = G_1 + G_2 + \dots + G_h$  and  $\mathbf{G}' = G'_1 + G'_2 + \dots + G'_h$ , we say that they are *isomorphic* if we can establish a one-to-one correspondence between the elements of  $\mathbf{G}$  and those of  $\mathbf{G}'$  such that the multiplication

rule is preserved. That is if  $G'_i \leftrightarrow G_i$ ,  $G'_j \leftrightarrow G_j$ ,  $G'_k \leftrightarrow G_k$  and  $G_i G_j = G_k$  then  $G'_i G'_j = G'_k$ . The group  $C_{3v}$  for instance, is isomorphic with the group whose elements are the two-dimensional matrices listed in Table IV (§ 1.7). The combination law in this latter group is the multiplication rule for matrices. If the correspondence between the two groups given is not one-to-one, but the multiplication rule is still preserved, we say that the two groups are *homomorphic*. Every group, for instance, is homomorphic to a group the elements of which are all unit matrices (see for example the Table IV).

### 2.3 Conjugation and Related Properties

If  $A$  and  $B$  are elements of a group  $G$  we say that  $A$  is *conjugate* to  $B$  ( $A \sim B$ ) if there is an element  $X \in G$  such that

$$A = X^{-1}BX.$$

The meaning of this definition is quite clear if we go from the above expression to the corresponding one for the representatives of the operators:  $D(A) = D(X)^{-1}D(B)D(X)$ . This means (§ 1.6) that, if  $\xi$  denotes the basis corresponding to  $D(B)$ ,  $D(A)$  represents the *same* operation, but in the basis  $X\xi$ . Conjugate operations are therefore identical operations, but performed in different systems of axes. As an example, notice that  $C_3^- = \sigma_1 C_3^+ \sigma_1 = \sigma_1^{-1} C_3^+ \sigma_1$  (cf. Table V, § 2.1). In fact,  $C_3^-$  is just the same operation as  $C_3^+$  except that it is performed after reflection of the axes in the symmetry plane  $\sigma_1$  (see Fig. 9 and remember that the positive sense of rotation is always that which takes  $x$  into  $y$ ).

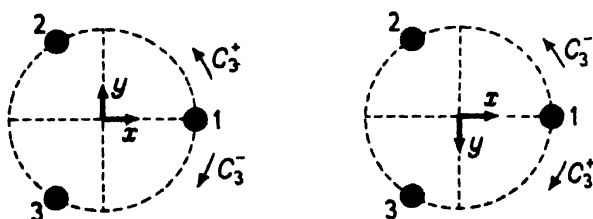


FIG. 9. Relation between the conjugate operations  $C_3^+$  and  $C_3^-$ .

It should be stressed that conjugation is a group property. That is,  $C_3^+$  and  $C_3^-$ , for instance, may be conjugate when considered as operations of a given group but not so when they are elements of a different one. In fact for the group  $C_3$  (see § 6.1) made up only of  $E$ ,  $C_3^+$  and  $C_3^-$  the two rotations are no longer conjugate because, as the reflection planes do not belong to the group, there is no operation that takes one rotation into the other.

The conjugation relation satisfies the same conditions that characterize an equality, that is, it possesses the reflexive, symmetric and transitive properties. The first one is obvious because  $A = E^{-1}AE$  and hence  $A \sim A$ . The proof of the symmetric property is simple and we shall leave it to the reader. An important consequence of this property is that we can now refer to two elements,  $A$  and  $B$ , as being conjugate among themselves.

In order to prove the transitive property we must show that if  $A \sim B$  and  $B \sim C$  then  $A \sim C$ . In fact, we have  $A = X^{-1}BX$  and  $B = Y^{-1}CY$  so that  $A = X^{-1}Y^{-1}CYX = (YX)^{-1}CYX$ . Now, as  $Y$  and  $X$  belong to  $G$ ,  $YX$  must also belong to  $G$  and hence  $A \sim C$ .

On account of the transitive property of conjugation, all the elements of a group that are conjugate to a given one,  $A$  say, are conjugate among themselves. Such a set of elements is called a *class*. The class  $\mathcal{C}_A$  to which  $A$  belongs is obtained most easily by taking all the products  $G_i^{-1}AG_i$ , ( $i = 1, 2, \dots, h$ ,  $h$  being the order of the group  $G$ ).

Let us find as an example the class to which the operation  $\sigma_1$  of  $C_{3v}$  belongs. In accordance with our previous considerations we should expect to find  $\sigma_2$  and  $\sigma_3$  in it, because they are just the same operation as  $\sigma_1$ , except that the axes are rotated by  $C_3^+$  and  $C_3^-$  respectively. In fact,

$$\begin{aligned} E^{-1}\sigma_1E &= E\sigma_1E = \sigma_1 \\ (C_3^+)^{-1}\sigma_1C_3^+ &= C_3^-\sigma_1C_3^+ = \sigma_2 \\ (C_3^-)^{-1}\sigma_1C_3^- &= C_3^+\sigma_1C_3^- = \sigma_3 \\ \sigma_1^{-1}\sigma_1\sigma_1 &= \sigma_1\sigma_1\sigma_1 = \sigma_1 \\ \sigma_2^{-1}\sigma_1\sigma_2 &= \sigma_2\sigma_1\sigma_2 = \sigma_3 \\ \sigma_3^{-1}\sigma_1\sigma_3 &= \sigma_3\sigma_1\sigma_3 = \sigma_3 \end{aligned}$$

The most general notation for the class  $\mathcal{C}_A$  to which  $A$  belongs is  $\mathcal{C}_A = \sum_i G_i^{-1}AG_i$ , where the summation sign is to be understood in the sense of the Galois notation (§ 2.2). If the group is abelian  $\mathcal{C}_A = \sum_i G_i^{-1}AG_i = \sum_i G_i^{-1}G_iA = \sum_i A$ , so that the class corresponding to any element contains the given element only.

An important property of a class is that of being invariant under conjugation. This means that if we take the complex  $\mathcal{C}_A = \sum_i G_i^{-1}AG_i$  and conjugate it under any element  $G_j$  of the group,  $G_j^{-1}\mathcal{C}_AG_j$  is still the same complex, except perhaps for the order. In fact,

$$G_j^{-1}\mathcal{C}_AG_j = \sum_i G_j^{-1}G_i^{-1}AG_iG_j.$$

$G_i G_j$  is always an element of the group, say  $G_k$ , and we can write  $\sum_i G_i G_j = \sum_k G_k$  because we have in both cases the same elements, at most in different order. That is,

$$\sum_i G_i^{-1} G_i^{-1} A G_i G_j = \sum_k G_k^{-1} A G_k = \sum_i G_i^{-1} A G_i = \mathcal{C}_A.$$

If a subgroup  $N$  of  $G$  happens to be a sum of classes, it is also invariant under conjugation and it is called an *invariant subgroup* or *normal divisor*. Conversely, any subgroup that is invariant under conjugation must be a sum of classes. Given an invariant subgroup  $N$  and any element  $X \in G$  we have  $X^{-1}NX = N$ , so that  $NX = XN$ , which shows that the right and left co-sets of an invariant subgroup are identical.

As an example,  $E + C_3^+ + C_3^- = C_3$  (cf. § 6.1 for the notation) is an invariant subgroup of  $C_{3v}$ , which is clear, as it is the sum of two classes. The invariant property could also be quickly determined from the multiplication table of the group (Table V, § 2.1) by noticing that the right and left co-sets of  $C_3$  are identical for all the elements of the group. In fact  $C_3\sigma_1 = \sigma_1 + \sigma_2 + \sigma_3$ ,  $\sigma_1 C_3 = \sigma_1 + \sigma_3 + \sigma_2$  and so on.

We shall now prove the following interesting property; given an invariant subgroup  $N$  of a group  $G$  of order  $h$ , the set of all its co-sets  $NG_i = G_i N$ ,  $i = 1, 2, \dots, h$ , forms a group. (Notice how general the definition of a group can be: the elements of the group we are considering are themselves sets.) This group is called the *factor group* of  $G$  with respect to  $N$  and it is denoted with the symbol  $G/N$ . We now prove that the four group postulates are satisfied for the factor group. In this proof we use the relation  $NN = N$ , which follows from the fact that  $N$  is a group and the standard definition of the product of complexes.

- (1) Existence of the product:  $NG_i NG_j = NNG_i G_j = NG_k \in G/N$ .
- (2) Associative property:  $NG_i (NG_j NG_k) = NG_i G G_k = (NG_i NG_j) NG_k$ .
- (3) Identity:  $N$  is the identity element of  $G/N$ . In fact

$$N(NG_i) = (NG_i)N = NNG_i = NG_i.$$

- (4) Inverse:  $NG_i NG_i^{-1} = NG_i G_i^{-1} N = NN = N \equiv E$ .

It should be noticed that an element of  $G$  may appear more than once in the factor group  $G/N = \sum_i NG_i$ . For instance, for all  $G_i \in N$ ,  $NG_i = N$ . Also, some co-sets such as  $NG_i$  and  $NG_j$  ( $G_i$  and  $G_j$  not in  $N$ ) can be identical. It is often convenient to take  $G/N$  as the set of all different terms in the (Galois) sum  $\sum_i NG_i$ . The elements  $G_i$  that appear in it are then called the *co-set representatives* of the factor group. (Notice that the meaning of the word representative here is different from the one it has in the expression

"representative of an operator".) As an example, the factor group  $C_{3v}/C_3$  is given by  $C_3 + C_3C^+ + C_3C^- + C_3\sigma_1 + C_3\sigma_2 + C_3\sigma_3 = C_3 + C_3\sigma_1$  (verify, by using Table V, § 2.1 that  $C_3\sigma_2 = C_3\sigma_3 = C_3\sigma_1$ ).

The last concept that we shall consider is that of the *product of classes* which will be found very useful later on. The product of two classes is just a product of complexes and, for future purposes, we shall here employ the exceptional definition of this product (see § 2.2). We shall now prove that *the product of two classes is a sum of classes*. Let us consider two classes  $\mathcal{C}_A$  and  $\mathcal{C}_B$ , given as follows:

$$\mathcal{C}_A = A_1 + A_2 + \dots + A_r,$$

$$\mathcal{C}_B = B_1 + B_2 + \dots + B_s.$$

To show that the product  $\mathcal{C}_A\mathcal{C}_B = \sum_{lm} A_l B_m$  is a sum of classes, we must prove that every element  $X^{-1}A_l B_m X$  conjugate to  $A_l B_m$  appears also in the sum (hence, if one element of a class belongs to the sum, the whole class appears in it). In fact,

$$X^{-1}A_l B_m X = X^{-1}A_l X X^{-1}B_m X.$$

$X^{-1}A_l X$  by definition belongs to  $\mathcal{C}_A$  and we can call it  $A_\lambda$ . Analogously  $X^{-1}B_m X = B_\mu$ . Hence  $X^{-1}A_l B_m X = A_\lambda B_\mu$  which is one of the terms in the sum  $\sum_{lm} A_l B_m$ .

As a result of the above theorem, we can write a product of two classes  $\mathcal{C}_A\mathcal{C}_B$  as follows:

$$\mathcal{C}_A\mathcal{C}_B = \sum_M c_{AB,M} \mathcal{C}_M, \quad (26)$$

where we sum over all the classes of a group. The coefficient  $c_{AB,M}$ , which gives the number of times the class  $M$  appears in the sum, can be different from unity because we use the exceptional definition of the product. The first two suffixes in it denote its dependence on the two classes that are multiplied. As an example, consider the class  $\sigma_1 + \sigma_2 + \sigma_3$  of  $C_{3v}$ , which we shall denote now with the symbol  $\mathcal{C}_\sigma$ .

$$\begin{aligned} \mathcal{C}_\sigma\mathcal{C}_\sigma &= (\sigma_1 + \sigma_2 + \sigma_3)(\sigma_1 + \sigma_2 + \sigma_3) \\ &= \sigma_1\sigma_1 + \sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_2\sigma_1 + \sigma_2\sigma_2 + \sigma_2\sigma_3 + \sigma_3\sigma_1 + \sigma_3\sigma_2 + \sigma_3\sigma_3 \\ &= E + C_3^- + C_3^+ + C_3^+ + E + C_3^- + C_3^- + C_3^+ + E \\ &= 3\mathcal{C}_E + 2\mathcal{C}_{C_3} \end{aligned}$$

where  $\mathcal{C}_{C_3}$  is the class  $C_3^+ + C_3^-$ . 3 and 2 here are the coefficients  $c_{AB,M}$  above.

### 3. Representations

We shall deal in this section with the representation of groups, for which an introduction was given in § 1. We shall now make full use of the methods of group theory so that we shall be able to provide an answer to the problems left unsolved at the end of § 1.

#### 3.1 Representations: Definitions

We gave in § 1 the definition of the matrix representatives of operators and we used the term "representation" just as a collective noun for a set of representatives, without a proper definition. This can now be provided. A *representation* of a group is a group of matrices homomorphic to it. This means that given the elements  $G_r$ ,  $G_s$  and  $G_r G_s$  of a group  $G$  we establish a correspondence between them and matrices  $D(G_r)$ ,  $D(G_s)$ ,  $D(G_r G_s)$ , respectively, not necessarily different, such that

$$D(G_r)D(G_s) = D(G_r G_s). \quad (27)$$

These matrices, therefore, reproduce the multiplication table of the group  $G$ . A trivial example of a representation is obtained when the unit matrix is correlated with each element of the given group. On the other hand, when the correspondence established is one-to-one (isomorphism) the representation is called *faithful*.

It should be noticed that the definition of a representation given here does not provide a technique to obtain one. For groups of operators, the representatives defined in § 1 in terms of a chosen basis satisfy (27) and form a representation, the matrices of which just give the transformation properties of the basis. However, although the ultimate purpose of much of the work done when using group theory is to study the transformation properties of a basis in this fashion, it is always possible and often most convenient to consider representations independently from their bases. We shall in fact provide a manipulative technique to this effect.

If we have a representation of a group  $G$  we can obtain another one by applying the same similarity transformation on each of its matrices. The transformed matrices still form a group and are homomorphic to  $G$  because the similarity transformation preserves the multiplication rule.

Given two representations, we can obtain a third one by forming the *direct sum* of the matrices of the representation. This means that we write  $2 \times 2$  block-diagonal matrices, the diagonal elements of which are the



matrices that correspond to the same group element in each one of the two given representations. We must therefore show that if

$$D^1(R)D^1(S) = D^1(T) \quad (28)$$

$$D^2(R)D^2(S) = D^2(T) \quad (29)$$

then:

$$\left\| \begin{array}{c} D^1(R) \\ D^2(R) \end{array} \right\| \left\| \begin{array}{c} D^1(S) \\ D^2(S) \end{array} \right\| = \left\| \begin{array}{c} D^1(T) \\ D^2(T) \end{array} \right\|. \quad (30)$$

The proof is immediate, because the ordinary matrix multiplication rule is valid for block-diagonal matrices (or more generally, for supermatrices). This proof can be readily extended for direct sums of any number of matrices. It is also straightforward to prove the converse result, namely that when a representation has the special block-diagonal form (30) in which the blocks in the same position in the diagonal have the same dimensionality, these blocks form a representation. The representation given splits therefore into as many representations as blocks.

We have seen (§ 1.6) that the matrix representatives of a group of symmetry operators are unitary. This is not necessarily the case for other groups, but it can be proved (see Wigner,<sup>1</sup> p. 81) that every representation can be taken to unitary form by means of a similarity transformation. In what follows we shall always assume that this has been done, i.e., that our matrices are unitary

### 3.2 Reduction of Representations

If we apply a similarity transformation to all the matrices of a representation and obtain a new one made up of matrices that have the same block-diagonal form, we say that the representation has been *reduced*. Thus defined, the reduction of a representation may look like a hopeless task, because finding the appropriate similarity transformation is far from obvious. We shall give, however, a purely formal matrix method to carry out this task (§ 3.5). On the other hand, if we refer a given matrix representation to its basis it is much easier to see how the problem could, at least in principle, be solved.

In fact, suppose that we have a basis of functions

$$\varphi_1^{(1)} \dots \varphi_{l_1}^{(1)}, \varphi_1^{(2)} \dots \varphi_{l_2}^{(2)}, \dots, \varphi_1^{(n)} \dots \varphi_{l_n}^{(n)} \quad (31)$$

and that they span a representation all the matrices of which have the form

$$\begin{array}{c} \leftarrow l_1 \rightarrow \\ D^1(R) \\ \\ D^2(R) \\ \\ \\ D^n(R) \end{array} \quad (32)$$

This means that the functions  $\varphi_1^{(i)} \dots \varphi_{l_i}^{(i)}$  ( $i = 1, \dots, n$ ) transform purely among themselves under *all* the operations of the group, i.e., the transform  $R\varphi_r^{(i)}$  is a linear combination of the functions  $\varphi_s^{(i)}$  only ( $s = 1, \dots, l_i$ ). This is expressed by saying that the functions with the same superscript in (31) build up (or *span*) an *invariant subspace* of the function space, i.e., a space such that every vector in it is transformed under every operation of the group into another vector of the same space. (The word vector, of course, is used here in the most general sense.)

In accordance with the above considerations, in order to reduce a representation we must transform its basis  $\varphi$  into a basis  $U\varphi$  which splits up into invariant subspaces. The corresponding matrices undertake the similarity transformation  $D(U)^{-1}D(R)D(U)$  and take the form (32). It was in this manner that we proceeded in § 1.7 to go from the reducible representation of Table II to that of Table III.

It should be noticed that when a representation is reduced as above, the matrices  $D^i(R)$  for all  $R$  and  $i = 1, \dots, n$  form  $n$  representations, as results from the theorem given at the end of § 3.1.

### 3.3 The Basis of a Representation: Expansion of an Arbitrary Function

We shall consider again the representations with reference to their bases. The latter were defined as complete orthonormal sets of functions and a technique should be given to obtain such sets. On doing this, we shall also be able to see how one of the problems set in the introduction to this chapter can in principle be solved. This is that of the expansion of an arbitrary function in terms of functions that belong to the various possible symmetry types. The actual technique for the solution will be left until § 5.

Consider an arbitrary function  $\phi$  and form its transforms  $R_i\phi$  under all the operations  $R_i$  of a group  $G$  of order  $h$ . For convenience, let us define  $\phi_i = R_i\phi$ . If the functions

$$\phi_1, \phi_2, \dots, \phi_h \quad (33)$$

are not all linearly independent we can choose out of them a linearly independent set

$$\phi_2, \dots, \phi_{k'}. \quad (34)$$

We can now show that this set spans a representation of the group. In fact, consider  $R_k \phi_m = R_k R_m \phi$ . We can write  $R_k R_m = R_l \in G$ , so that  $R_k \phi_m = R_l \phi$ . This function belongs to the set (33) so that it is either one of the functions of the set (34) or a linear combination of them such as

$$R_k \phi_m = \sum_n \phi_n \Delta_{nm}.$$

Clearly, the coefficients  $\Delta_{nm}$  form a matrix  $\Delta$  which is a representative of  $R_k$ . Analogously the other representatives, and hence the representation, can be obtained.

Suppose now that we can obtain a matrix  $U$  that reduces completely the representation spanned by the basis  $\langle \phi_1 \phi_2 \dots \phi_{k'} |$ . Therefore

$$\langle \phi_1 \phi_2 \dots \phi_{k'} | U = \langle \phi_1^{(1)} \dots; \phi_1^{(2)} \dots; \dots; \phi_1^{(n)} \dots$$

where, as before, the superscript denotes the irreducible representation or symmetry type to which the function belongs. We can now write

$$\langle \phi_1 \phi_2 \dots \phi_{k'} | = \langle \phi_1^{(1)} \dots; \phi_1^{(2)} \dots; \dots; \phi_1^{(n)} \dots | U^{-1}. \quad (35)$$

If  $R_1$  is the identity operation,  $\phi_1 = \phi$ , the function from which we started. Therefore Eq. (35) in its expanded form shows that the original function  $\phi$  can be given as a linear combination of the functions  $\phi_1^{(1)} \dots \phi_1^{(n)}$  that belong to the various irreducible representations of the group. The coefficients of this expansion are the elements of the first column of the matrix  $U^{-1}$ . As we shall give in § 3.5 a method to find the matrix  $U$  that reduces the representation, the problem of expanding a function in terms of the functions of the various symmetry types can be considered as solved. A more direct method will be given in § 5.

It should be noticed that the method given here to construct a basis for the representation of a group is in fact that implicitly used in § 1.7. The functions  $\phi_1, \phi_2, \phi_3$  therein used can all be obtained from  $\phi_1$  (that takes the place of our  $\phi$ ) as follows:  $E\phi_1 = \phi_1, \sigma_1\phi_1 = \phi_1, \sigma_2\phi_1 = \phi_3, \sigma_3\phi_1 = \phi_2, C^+\phi_1 = \phi_3, C^-\phi_1 = \phi_2$  (see Table I, § 1.7). From this set of linearly dependent functions we extract the functions  $\phi_1, \phi_2, \phi_3$ , which is the linearly independent set that we have used.

### 3.4 The Schrödinger Equation

A very important case when the basic functions span a reduced representation of the form (32) arises when the eigenfunctions of the Hamiltonian are used to form a basis.

The Hamiltonian, and therefore the Schrödinger equation is invariant under operations that can be broadly classified in two types. First, we must consider the transformations of the system of axes with respect to which the Hamiltonian is written. These are straightforward symmetry operations, considered in § 1.1. Secondly, to write down the Hamiltonian we must label the various particles that make up the system. Since the energy and hence the Hamiltonian cannot change when the labels of identical particles are interchanged, the Hamiltonian is invariant under the *permutation* of identical particles, such as electrons.

It is simple to show that the operations just considered form a group. This is called the *group of the Schrödinger equation*.

Let us go back to a basis of functions of the form (31). Assume now that the  $\varphi$ 's are solutions of the Schrödinger equation and that their superscripts have been used to indicate the energy eigenvalue to which they belong. Eigenfunctions that have the same superscript are degenerate and it is clear that they span an invariant subspace of the space of solutions of the Schrödinger equation. This is so because, if  $R$  is an operation of the Schrödinger group  $R\varphi_r^{(i)}$  must be a function belonging to the same energy eigenvalue as  $\varphi_r^{(i)}$  since an operation of the Schrödinger group cannot affect the energy.  $R\varphi_r^{(i)}$  is therefore degenerate with the functions  $\varphi_1^{(i)}, \dots, \varphi_l^{(i)}$  and must be expressible as a linear combination of them. Therefore, the representation spanned by the eigenfunctions of the Schrödinger equation will have the block-diagonal form (32), each block corresponding to an energy eigenvalue.

This result shows that to each eigenvalue of the energy there corresponds a representation of the Schrödinger group. In most cases this representation is also irreducible, because otherwise we would have two independent subspaces, that is, two linearly independent sets of functions that belong to the same eigenvalue. Although this is possible, it is not the most common type of degeneracy and it is usually referred to as *accidental degeneracy* (see § 1.2). All other cases of degeneracy originate in some symmetry property of the system.

Summarizing: each eigenvalue of the energy corresponds to an irreducible representation of the Schrödinger group, except for cases of accidental degeneracy. It is also clear that in every case a formal study of the

Schrödinger group so as to find the number and dimensions of its irreducible representations will indicate the number of energy levels and their degree of degeneracy. This shows the power of the group-theoretical methods in the treatment of degeneracy.

### 3.5 A Criterion for Reducibility\*

We shall provide in this section a criterion to find when a given representation is reducible, as well as a method of reducing it, when this is possible. These results arise from the following:

*Theorem 1.* Given a matrix  $M$  that commutes with all the matrices of a representation, then: (1) if the representation is irreducible  $M$  must be a constant matrix (that is, a multiple of the unit matrix); (2) if  $M$  is nonconstant, the representation is reducible and the matrix  $U$  that diagonalizes  $M$  is the matrix that reduces the representation.

From the second part of the theorem we see that if there is no nonconstant matrix that commutes with a representation, this is irreducible. Hence, the following

*Corollary.* If every matrix that commutes with all the matrices of a representation is a constant matrix, the representation is irreducible.

The proof of theorem 1 requires a general property of matrices which we shall demonstrate first.

*Theorem 2.* Let  $D$  be a diagonal supermatrix (see § 1.6), the elements of which are constant matrices. Then every matrix  $S$  that commutes with it must be a diagonal supermatrix of the same structure (that is, if  $l_1, l_2, \dots, l_n$  are the dimensions of the elements of  $D$ , these, in the same order, are also the dimensions of the elements of  $S$ ).  $D$  and  $S$  have therefore the following forms:

$$D = \begin{pmatrix} D_1^{(1)} & & & \\ \swarrow l_1 & D_2^{(1)} & & \\ & \swarrow l_2 & D_3^{(1)} & \\ & & \ddots & \\ & & & D_i^{(n)} \\ & & & \swarrow l_n & D_n^{(n)} \end{pmatrix} \quad S = \begin{pmatrix} \leftarrow l_1 \rightarrow & & & \\ & \leftarrow l_2 \rightarrow & & \\ & & \ddots & \\ & & & \leftarrow l_n \rightarrow \end{pmatrix}$$

\* The proofs in this and the next two sections follow very closely those given by Wigner.<sup>1</sup>

All elements in  $D$  that have the same superscript, i.e., that belong to the same "element" of the supermatrix (each element being a constant matrix) are identical. The suffix used is given to number the matrix elements, when necessary, in the normal manner.

Particular cases of the above theorem are (1)  $S$  can be diagonal (in fact, two diagonal matrices always commute). (2) If  $l_1 = l_2 = \dots = l_n = 1$  (i.e., all the diagonal elements of  $D$  are different)  $S$  *must* be diagonal.

The proof of theorem 2 is as follows: The matrix equality

$$SD = DS$$

requires that of the corresponding matrix elements

$$\sum_r S_{ir} D_{rj} = \sum_r D_{ir} S_{rj}.$$

As  $D$  is diagonal,  $D_{rj} \neq 0$  only when  $r = j$  and  $D_{ir} \neq 0$  only when  $r = i$ , so that

$$S_{ij} D_j = D_i S_{ij}.$$

Hence  $S_{ij}(D_j - D_i) = 0$ . (Notice that as we do not use here the superscript notation,  $D_i$  and  $D_j$ , are matrix elements in the ordinary sense, i.e., they can be, for instance, two elements belonging to the same block in the diagonal). Therefore, if  $D_i \neq D_j$ ,  $S_{ij} = 0$ .  $D_j$  is different from  $D_i$  for a matrix element such as the one marked with a dot in the matrix  $D$  given above. It is therefore clear that the matrix  $S$  has the shape shown before, which proves the theorem.

We can now prove theorem 1. We shall first show that it is enough to prove it for the case when  $M$  is a Hermitian matrix. In fact, let us assume that an arbitrary matrix  $M$  commutes with all the matrices of a representation

$$D(R)M = MD(R). \quad (36)$$

for all  $R$  in  $\mathfrak{G}$ . The adjoint of this equality is

$$D(R)^\dagger M^\dagger = M^\dagger D(R)^\dagger.$$

As the representation is unitary ( $D(R)^\dagger D(R) = D(R)D(R)^\dagger = 1$ ) we obtain, on multiplying each side on the left and on the right by  $D(R)$ ,

$$M^\dagger D(R) = D(R)M^\dagger.$$

This shows that, if  $M$  commutes with the matrices of the representation so does  $M^\dagger$ . Therefore, the following two Hermitian matrices possess the same property

$$H_1 = M + M^\dagger \quad H_2 = i(M - M^\dagger).$$

Since  $M = \frac{1}{2}(H_1 - iH_2)$ , we have proved that any matrix that commutes with all the matrices of a representation can be expressed in terms of Hermitian matrices that satisfy the same condition. It is then enough to prove the theorem for an arbitrary Hermitian matrix.

Consider now the matrix  $M$  in (36) to be Hermitian. Therefore, we can take it into diagonal form  $d$  with a unitary matrix  $U$ :  $d = U^{-1}MU$ .

Let us apply the same unitary transformation on the matrices of the representation. If we call  $U^{-1}D(R)U = D_U(R)$ , the invariance of the product under unitary transformations gives, from (36),

$$D_U(R)d = dD_U(R) \quad (37)$$

for all  $R$  in  $\mathfrak{G}$ . The matrix  $D_U(R)$  here takes the place of the matrix  $S$  in theorem 2 above. From this theorem, if  $M$  (and therefore  $d$ ) are not constant,  $D_U(R)$  must be a diagonal supermatrix (or block-diagonal matrix) which has the same structure as  $d$ . As this must be the case for all  $R$ , the representation is reduced. This proves the second part of theorem 1. It is also clear that, for the representation to be irreducible,  $d$  must have only one block, i.e., it must be a constant matrix, and so must also  $M = U d U^{-1}$ . This proves the first part of the theorem.

Much of the usefulness of theorem 1 arises from the fact that it is easy to find a matrix that commutes with those of a representation: it is enough to form the sum of the matrices of a class. In fact, a class  $\mathcal{C}_R$  can be written as  $\sum_{R \in \mathcal{C}_R} R$  (Galois summation). As this is invariant under conjugation we have  $X(\sum R) = (\sum R)X$  for all  $X$  in  $\mathfrak{G}$ . The matrix representatives preserve the algebraic rules, so that  $D(X)(\sum D(R)) = (\sum D(R))D(X)$  for all  $X$  in  $\mathfrak{G}$ . (Ordinary summation here).

As an example, consider the representation given in Table II (§ 1.7) for the group  $C_{3v}$ . The sum of the matrices of the class formed by  $C_3^+$  and  $C_3^-$  is:

$$\left\| \begin{array}{cc} 1 & \\ & 1 \\ 1 & \end{array} \right\| + \left\| \begin{array}{cc} & 1 \\ 1 & \\ & 1 \end{array} \right\| = \left\| \begin{array}{cc} 1 & 1 \\ 1 & 1 \\ 1 & 1 \end{array} \right\|$$

Therefore, the representation is reducible. To reduce it we obtain the matrix that diagonalizes the matrix on the right of the above expression. (To do this it is sufficient to find the eigenvectors of this matrix and to normalize them so as to make the resulting matrix unitary.) This is

$$U = \left\| \begin{array}{ccc} 1/\sqrt{3} & -1/\sqrt{3} & 0 \\ 1/\sqrt{3} & 1/\sqrt{6} & -1/\sqrt{2} \\ 1/\sqrt{3} & 1/\sqrt{6} & 1/\sqrt{2} \end{array} \right\|$$

It is now straightforward to verify that, when the matrices of Table II are transformed under a similarity with the matrix  $U$ , they take the reduced form given in Table III (§ 1.7). If we want to see whether the two-dimensional representation thus obtained (Table IV) is still further reducible, we apply our test again. The sum of the matrices  $D(C_3^+)$  and  $D(C_3^-)$  is

$$\begin{array}{ccc} -\frac{1}{2} & \frac{1}{2}\sqrt{3} & \\ & + & \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} & \end{array} \quad \begin{array}{ccc} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} & -1 \\ & + & \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & -1 \end{array}$$

and in fact we shall see in § 3.9 that the representation is irreducible.

### 3.6 Schur's Lemma\*

The theorem given in this section, due to Schur, will find an immediate application in the proof of the orthogonality relations given in § 3.7, which are the central point of representation theory.

Consider two irreducible representations of a group  $G$ , the matrices of which,  $D^1(R)$  and  $D^2(R)$  (all  $R$  in  $G$ ) are of dimension  $l_1$  and  $l_2$  respectively. If there is a matrix  $M$  (of  $l_1$  columns and  $l_2$  rows) such that

$$MD^1(R) = D^2(R)M, \text{ for all } R \text{ in } G, \quad (39)$$

then: (1) If  $l_1 = l_2$  either  $M$  is the null matrix or a nonsingular one, in which latter case  $M$  has an inverse and the two representations  $D^1(R)$  and  $D^2(R)$  are equivalent. (2) If  $l_1 \neq l_2$ ,  $M = 0$  (the null matrix).

*Proof.* We shall assume the representations to be unitary,  $D(R)^\dagger = D(R^{-1})$ , so that the adjoint of Eq. (39) is

$$D^1(R^{-1})M^\dagger = M^\dagger D^2(R^{-1}). \quad (40)$$

Multiply this expression by  $M$  on the left.

$$MD^1(R^{-1})M^\dagger = MM^\dagger D^2(R^{-1}).$$

From (39) (remember that  $R^{-1} \in G$ ),

$$D^2(R^{-1})MM^\dagger = MM^\dagger D^2(R^{-1}), \quad (\text{all } R \in G). \quad (41)$$

This shows that the (Hermitian) matrix  $MM^\dagger$  commutes with all the matrices of the representation  $D^2$  and therefore, from theorem 1 of § 3.5,  $MM^\dagger = c1$ .

Consider now the case  $l_1 = l_2$ ; there are two possibilities.

1.  $c \neq 0$ , therefore the determinant  $|c1| \equiv c^l \neq 0$ . This means, from the relation  $MM^\dagger = c1$ , that  $|M| \neq 0$ . Hence,  $M$  is nonsingular and we

\* The proofs in this section and the following one are not essential in a first reading.



can multiply Eq. (39) on the left by  $M^{-1}$ , so that  $D^1(R) = M^{-1}D^2(R)M$ , and the two representations are equivalent.

2.  $c = 0$ , then  $MM^\dagger = 0$ . Hence  $\sum_j M_{ij} M_{ji}^\dagger \equiv \sum_j M_{ij} M_{ij}^* = 0$ . The last sum is positive definite, so that we must have  $M_{ij} = 0$  for all  $i, j$ . Therefore  $M = 0$ .

When  $l_1 \neq l_2$  we can always assume that  $l_1 < l_2$ , so that a square matrix  $N$  can be formed by adding  $l_2 - l_1$  null columns to  $M$ .

$$N = \begin{array}{c} \uparrow \\ \parallel \\ \leftarrow l_1 \rightarrow \quad \leftarrow l_2 - l_1 \rightarrow \\ \begin{array}{cc} 0 \dots 0 \\ 0 \dots 0 \\ \vdots \\ \vdots \\ 0 \dots 0 \end{array} \\ \parallel \\ \downarrow \end{array} \quad \begin{array}{c} M \\ \vdots \\ \vdots \\ \vdots \end{array}$$

It can be seen at once that  $NN^\dagger = MM^\dagger$ . Also  $|N| = 0$ , hence  $|MM^\dagger| = 0$ . Therefore  $|c1| = 0$ , so that  $c = 0$ . As before,  $M = 0$ .

### 3.7 The Orthogonality Relations

Consider two irreducible, nonequivalent (but perhaps identical) representations of a group  $G$ . The elements of their matrix representatives satisfy a very important and simple orthogonality property, namely that

$$\sum_R D^i(R)_{rs}^* D^j(R)_{tu} = \frac{h}{\sqrt{l_i l_j}} \delta_{ij} \delta_{rt} \delta_{su}, \quad (42)$$

where  $h$  is the order of  $G$  and  $l_i$  and  $l_j$  are the dimensions of the representations.

*Proof.* We shall first form a matrix  $M$  that satisfies the relation

$$D^i(S)M = MD^i(S) \quad (43)$$

for all  $S \in G$ . In fact, define  $M = \sum_R D^j(R) X D^i(R)^{-1}$  where  $X$  is an arbitrary matrix of  $l_j$  rows and  $l_i$  columns.

$$\begin{aligned} D^i(S)M &= \sum_R D^i(S) D^j(R) X D^i(R)^{-1} \\ &= \sum_R D^i(SR) X D^i(SR)^{-1} D^i(S) \\ &= \left[ \sum_{(SR)} D^i(SR) X D^i(SR)^{-1} \right] D^i(S) \\ &= MD^i(S). \end{aligned}$$

A matrix element  $M_{tr}$  of  $M$  is given by

$$M_{tr} = \sum_{kl} \sum_R D^i(R)_{tk} X_{kl} D^i(R)^{-1}_{lr}.$$

As the matrix  $X$  is arbitrary we make the convenient choice  $X_{kl} = 0$  except  $X_{ss} = 1$ . Therefore

$$M_{tr} = \sum D^i(R)_{tu} D^i(R)^{-1}_{sr} = \sum D^i(R)^*_{rs} D^i(R)_{tu}. \quad (44)$$

When  $i \neq j$  we can apply Schur's lemma to expression (43). This shows that either  $M = 0$  or  $D^i$  and  $D^j$  are equivalent. As this latter alternative contradicts the hypothesis,  $M = 0$  and from (44)

$$\sum D^i(R)^*_{rs} D^j(R)_{tu} = 0 \quad \text{if} \quad i \neq j \quad (45)$$

When  $i = j$ , expression (43) shows that  $M$  commutes with all the matrices of an irreducible representation and hence, from theorem 1 of § 3.5 it must be a constant matrix

$$M_{tr} = c_{su} \delta_{rt}. \quad (46)$$

Here, bearing in mind (44), we call  $c_{su}$  the diagonal element of  $M$ . To determine it we take  $t = r$  in the last expression and sum over  $t$  up to  $l_i$ :

$$\sum_t^{l_i} M_{tt} = \sum_t^{l_i} c_{su} = l_i c_{su}. \quad (47)$$

On the other hand, from (44)

$$\sum_t M_{tt} = \sum_t \sum_R D^i(R^{-1})_{st} D^i(R)_{tu} = \sum D^i(E)_{su} = h \delta_{su}. \quad (48)$$

Therefore  $c_{su} = (h/l_i) \delta_{su}$ .

Equation (46) can now be written as

$$\sum_R D^i(R)^*_{rs} D^j(R)_{tu} = \frac{h}{\sqrt{l_i l_j}} \delta_{rt} \delta_{su}. \quad (49)$$

On combining this equation with (45), Eq. (42) and the theorem are proved.

## 3.8 Consequences of the Orthogonality Relation

The orthogonality relation (42) of § 3.7 acquires a more direct meaning when interpreted as follows. If we pick up from each matrix of a representation an element belonging to a given row and column, we obtain a vector of dimension  $h$ , this being the order of the group. Equation (42) states that any two such vectors are orthogonal. As an example, consider the representations given in Table IV of § 1.7. Let us denote with 1 and 2 the first and second representation respectively listed in the table. Two of the vectors just described are, in the notation of (42):

$$\begin{aligned} r = 1, \quad s = 1 & \quad (1, 1, 1, 1, 1, 1) \\ r = 2, \quad s = 2 & \quad (0, 0, -\frac{1}{2}\sqrt{3}, \frac{1}{2}\sqrt{3}, \frac{1}{2}\sqrt{3}, -\frac{1}{2}\sqrt{3}) \end{aligned}$$

Then

$$\sum_R D^1(R)_{11}^* D^2(R)_{12} = 0 + 0 - \frac{1}{2}\sqrt{3} + \frac{1}{2}\sqrt{3} + \frac{1}{2}\sqrt{3} - \frac{1}{2}\sqrt{3} = 0$$

$$\sum_R D^2(R)_{12}^* D^2(R)_{12} = \frac{6}{2}$$

as expected.

If  $l_1, l_2, \dots, l_n$  are the dimensions of the  $n$  irreducible representations of a group, we can build up in the manner just described  $l_1^2 + l_2^2 + \dots + l_n^2$ ,  $h$ -dimensional vectors. As there are at most  $h$  orthogonal vectors in a space of  $h$  dimensions, we see that  $\sum l_i^2 \leq h$ . It can be proved that the equality sign holds:

$$\sum_{i=1}^{n_i} l_i^2 = h. \quad (50)$$

That is, *the sum of the squares of the dimensions of the irreducible representations of a group is equal to its order.*

As an application of this result, consider again the group  $C_{3v}$  for which we gave two representations in Table IV, § 1.7, of dimensions 1 and 2 respectively. We then have  $1^2 + 2^2 = 5$ , whereas the order of the group is 6. Therefore  $C_{3v}$  must possess another one-dimensional representation. We thus answer the second question formulated at the end of § 1.

It should be noted that the main use of Eq. (50) is not the one just given, but that of finding the dimensions of the irreducible representations of

a group. This is so because there is a very simple rule to find the number of irreducible representations of a group. (See § 3.9.) This rule shows for instance that the group  $C_{3v}$  has three irreducible representations. Equation (50) then takes the form  $l_1^2 + l_2^2 + l_3^2 = 6$  and it is easy to find by trial and error that this is satisfied by  $l_1 = 1$ ,  $l_2 = 1$  and  $l_3 = 2$ .

### 3.9 The Characters

The matrix representatives permit us to obtain a certain degree of independence from the bases on which they are defined. In fact, once a representation is obtained, much useful manipulation can be carried out without a reference to the basis of the representation. However, the fact remains that the representation itself depends on the basis, so that whenever this is changed an unitary transformation is effected on the representation.

To go one step further, so as to be able to dispense altogether with the basis of the representation, we must characterize this latter by a quantity that is invariant under a unitary transformation. Matrices possess two invariants under similarity transformations. They are the determinant of the matrix (product of its eigenvalues) and its trace (sum of the eigenvalues). It is simple to prove that the trace of a matrix is invariant under a similarity transformation. The *trace*  $\text{Tr}(\alpha)$  of a matrix  $\alpha$ , is defined as the sum of its diagonal elements,

$$\text{Tr}(\alpha) = \sum_i \alpha_{ii}.$$

Therefore, the trace of the product of two matrices does not depend on the order in which they are multiplied.

$$\text{Tr}(\alpha\beta) = \sum_i (\alpha\beta)_{ii} = \sum_{ij} \alpha_{ij}\beta_{ji} = \sum_{ji} \beta_{ji}\alpha_{ij} = \sum_j (\beta\alpha)_{jj} = \text{Tr}(\beta\alpha).$$

Now

$$\text{Tr}(\beta^{-1}\alpha\beta) = \text{Tr}(\beta^{-1}\beta\alpha) = \text{Tr}(\alpha), \quad (51)$$

which proves the invariance property discussed.

In representation theory the trace of a matrix representative of an element  $R$  of a group is called the *character* of this element, and we shall denote it with the symbol  $\chi(R)$ . The set of characters of a representation is independent of the basis used. Also, (51) shows that the characters of all the elements of a class are identical.

As an example, it can be easily seen that the characters of the (equivalent) representations given in Tables II and III of § 1.7 are the same:

$$\begin{array}{ccc} E & \sigma_1, \sigma_2, \sigma_3 & C_3^+, C_3^- \\ 3 & 1 & 0 \end{array} \quad (52)$$

Notice that the character of the identity is always equal to the dimension of the representation.

The orthogonality property of the matrix elements of irreducible representations results in an analogous one for the characters

$$\sum_R \chi^i(R)^* \chi^j(R) = h \delta_{ij} \quad (53)$$

(Notice that this expression is only valid when  $i$  and  $j$  are irreducible representations.) In fact,

$$\begin{aligned} \chi^i(R)^* &= \sum_{\nu=1}^{l_i} D^i(R)_{\nu\nu}^*, \\ \chi^j(R) &= \sum_{\mu=1}^{l_j} D^j(R)_{\mu\mu}. \end{aligned}$$

On multiplying out these two expressions and summing over all  $R$ , we obtain

$$\begin{aligned} \sum_R \chi^i(R)^* \chi^j(R) &= \sum_{\mu\nu} \sum_R D^i(R)_{\nu\nu}^* D^j(R)_{\mu\mu} \\ &= \sum_{\mu\nu} \frac{h}{l_i l_j} \delta_{ij} \delta_{\mu\nu} = \sum_{\mu=1}^{l_j} \frac{h}{l_j} \delta_{ij} = h \delta_{ij}. \end{aligned}$$

We use here the orthogonality relation (42) of § 3.7. It is often convenient to write Eq. (53) in the form

$$\sum_{\mathcal{C}} h_{\mathcal{C}} \chi^i(\mathcal{C})^* \chi^j(\mathcal{C}) = h \delta_{ij}, \quad (54)$$

where  $h_{\mathcal{C}}$  is the number of elements in the class  $\mathcal{C}$ .

Relation (53) expresses the fact that, when the characters for all operations of a group are considered as forming an  $h$ -dimensional vector, these vectors are orthogonal. As an example, consider the two representations of  $C_{3v}$  given in Table IV, § 1.7. We list the corresponding characters in Table VI.

TABLE VI  
CHARACTERS OF THE REPRESENTATIONS OF  $C_{3v}$  GIVEN IN TABLE IV<sup>a</sup>

Representation	$E$	$3\sigma$	$2C_3$
1-dimensional	1	1	1
2-dimensional	2	0	-1

<sup>a</sup> The numerals before the symbols for the operations are the number of elements  $h_{\mathcal{C}}$  in the class  $\mathcal{C}$ .

We shall prove later on in this section that the two-dimensional representation given in Table VI is irreducible, so that Eq. (54) can be used. We immediately verify that the characters of the two representations listed in Table VI are orthogonal:

$$1 \times 1 \times 2 + 3 \times 2 \times 0 + 2 \times 1 \times (-1) = 0.$$

The main use of the orthogonality relation of the characters arises in the solution of the following problem. We gave in Table II of § 1.7 a reducible representation of  $C_{3v}$ , which we found we could reduce (by a similarity transformation explicitly given in § 3.5<sup>f</sup>) into the two representations just listed. In practice we usually possess character tables for all the irreducible representations of a group (see § 3.10) and it is often important to be able to predict, without actually carrying out the process of reduction, how many times each irreducible representation of the group will be contained in a given, reducible one. We shall now see how this can be done.

Suppose that we reduce a representation  $D(R)$ . Its matrices will then take block-diagonal form  $D'(R)$ , which can be written symbolically as

$$D'(R) = \sum_j a^{(j)} D^{(j)}(R). \quad (55)$$

Here the coefficient  $a^{(j)}$  gives the number of times that the irreducible representation  $D^{(j)}$  is contained in  $D$ . (Notice that the summation sign in (55) denotes a direct sum of matrices). As we go from  $D$  to  $D'$  through a similarity transformation,  $\chi[D'(R)] = \chi[D(R)]$ . Also, it is clear from (55) that for all operations  $R$  in a class  $\mathcal{C}$  we can write for the character  $\chi(\mathcal{C})$  of the reducible representation:

$$\chi(\mathcal{C}) = \sum_j a^{(j)} \chi^{(j)}(\mathcal{C}) \quad (56)$$

where  $\chi^{(j)}(\mathcal{C})$  is the character of the class  $\mathcal{C}$  in the  $j$ th irreducible representation.

We now multiply both sides of (56) by  $h_{\mathcal{C}}\chi^i(\mathcal{C})^*$ , add up over all the classes of the group and use the orthogonality condition (54). Then,

$$a^{(i)} = \frac{1}{h} \sum_{\mathcal{C}} h_{\mathcal{C}} \chi^i(\mathcal{C})^* \chi(\mathcal{C}) \quad (57)$$

which is the expression sought

As an example of the use of this expression we obtain the number of times the two-dimensional representation of  $C_{3v}$  (Table VI) is contained in the reducible one (see 52)

$$\frac{1}{6}[1 \times 2 \times 3 + 3 \times 0 \times 1 + 2 \times (-1) \times 0] = 1,$$

which agrees with the result obtained. In practice, of course, we would use a character table independently obtained by the method given in the following section

The orthogonality relation (54) yields a simple criterion for determining whether a given representation is irreducible or not. *The necessary and sufficient condition for a representation to be irreducible is that its characters satisfy the relation  $\sum_{\mathcal{C}} h_{\mathcal{C}} \chi^i(\mathcal{C})^* \chi^j(\mathcal{C}) = h$ .* That this condition is necessary results at once from (54). To show that it is sufficient, assume that the representation is reduced, so that

$$\chi^i(\mathcal{C}) = \sum_r a^{(r)} \chi^{(r)}(\mathcal{C}).$$

Hence,

$$\chi^i(\mathcal{C})^* \chi^j(\mathcal{C}) = \sum_{rs} a^{(r)} a^{(s)} \chi^{(r)}(\mathcal{C})^* \chi^{(s)}(\mathcal{C}).$$

Therefore,

$$\begin{aligned} \sum_{\mathcal{C}} h_{\mathcal{C}} \chi^i(\mathcal{C})^* \chi^j(\mathcal{C}) &= \sum_{rs} a^{(r)} a^{(s)} \sum_{\mathcal{C}} h_{\mathcal{C}} \chi^{(r)}(\mathcal{C})^* \chi^{(s)}(\mathcal{C}) \\ &= \sum_{rs} a^{(r)} a^{(s)} h \delta_{rs} = h \sum_r (a^{(r)})^2. \end{aligned}$$

Therefore, if

$$\sum_{\mathcal{C}} h_{\mathcal{C}} \chi^i(\mathcal{C})^* \chi^i(\mathcal{C}) = h,$$

$\sum_r (a^{(r)})^2$  must be equal to unity. For this to happen, all the integers  $a^{(r)}$  must cancel out, except one of them that must be equal to unity. Hence,

the representation is irreducible, which proves the sufficiency of the condition. We have, as an example, for the two-dimensional representation of Table VI:  $1 \times 2^2 + 3 \times 0^2 + 2 \times (-1)^2 = 6$ , which is the order of  $C_{3v}$ . Hence the representation is irreducible. This answers one of the questions formulated at the end of § 1.

The orthogonality relation of the characters has another important consequence. We see from Eq. (54) that the normalized characters  $\sqrt{(h_{\mathcal{C}}/h)}\chi'(\mathcal{C})$  form a system of orthonormal vectors. If  $n_{\mathcal{C}}$  is the number of classes of the group these vectors are  $n$ -dimensional. Their number, on the other hand, is just that of the irreducible representations of the group,  $n_i$ . The number of orthogonal vectors  $n_i$  must be no larger than their dimensionality  $n$ , so that  $n_i \leq n_{\mathcal{C}}$ . It can in fact be proved that the equality sign holds, i.e., that *the number of irreducible representations of a group is equal to the number of its classes*. In  $C_{3v}$  for instance we have three classes and we must have three irreducible representations. This confirms our previous result (§ 3.8) and answers finally the second of the questions proposed at the end of § 1. As shown in § 3.8, from the knowledge that the group  $C_{3v}$  admits three irreducible representations and the fact that the sum of the squares of their dimensions must be equal to the order of the group, we can infer that the dimensionalities of the irreducible representations of  $C_{3v}$  are 2, 1, 1. Therefore, we must still obtain one one-dimensional representation, which we shall do in the next section.

It will be useful for this purpose to bear in mind the following property of the characters. *If the characters of a representation are real they are also integral*. To prove this result it is enough to consider one matrix of a given class, which can be assumed, as we always do, to be unitary. Such a matrix can always be diagonalized, without altering its character. The diagonal elements are now the eigenvalues of the original matrix, the absolute value of which is equal to unity, because the matrix is unitary.\* Therefore, if they are real they must be either  $+1$  or  $-1$  so that the character must be an integer.

### 3.10 The Calculation of the Characters

The calculation of the characters of all the irreducible representations of a group can be done by using the following theorem, due to Burnside:

\* For a unitary matrix  $U^\dagger U = 1$ . Therefore  $\sum_j U_{ij}^\dagger U_{j\ell} = \sum_j U_{j\ell}^* U_{ji} = 1$ . When the matrix is taken to diagonal form, the left-hand side of this equality will be reduced to  $U_{ii}^* U_{ii} = 1$ . Hence  $|U_{ii}| = 1$ .



Suppose that two classes  $\mathcal{C}_A$  and  $\mathcal{C}_B$  of order  $h_A$  and  $h_B$  respectively are given, such that their product (§ 2.3) is

$$\mathcal{C}_A \mathcal{C}_B = \sum_M c_{AB,M} \mathcal{C}_M. \quad (58)$$

Call  $\chi_A = \chi(\mathcal{C}_A)$  and  $\chi_B = \chi(\mathcal{C}_B)$  the characters that correspond, in the same irreducible representation, to the classes considered. Then, the following relation holds between these characters:

$$h_A \frac{\chi_A}{\chi_E} h_B \frac{\chi_B}{\chi_E} = \sum_M c_{AB,M} h_M \frac{\chi_M}{\chi_E} \quad (59)$$

Here  $\chi_E$ , the character of the identity operation, is just the dimension of the representation considered

*Proof* Call  $C_A$  the matrix which is the sum of all the matrices that correspond to the operations of  $\mathcal{C}_A$  in the irreducible representation considered. This matrix commutes with all those of the representation (see § 3.5) so that it must be a constant matrix (§ 3.5).

$$C_A = \eta_A \mathbf{1} \equiv \begin{matrix} & \uparrow \\ \eta_A & \\ \eta_A & \chi_E \end{matrix} \quad (60)$$

$\eta_A \parallel \downarrow$

Therefore, on taking representatives in (58), we have:

$$\eta_A \eta_B = \sum_M c_{AB,M} \eta_M \quad (61)$$

The constant  $\eta_A$  can be easily determined. From (60):

$$\text{Tr}(C_A) = \chi_E \eta_A.$$

On the other hand, as  $C_A$  is the sum of the  $h_A$  matrices of the class, the character of which is  $\chi_A$ , we have:  $\text{Tr}(C_A) = h_A \chi_A$ . Hence  $\eta_A = h_A \chi_A / \chi_E$ . On introducing this value in (61), Eq. (59) is proved.

An example will show how the theorem is used to calculate the characters of irreducible representations. Again, we consider the group  $C_{3v}$ , which has the classes  $\mathcal{C}_E$ ,  $\mathcal{C}_{C_2}$ ,  $\mathcal{C}_\sigma$ . The number of elements in them is  $h_E = 1$ ,  $h_{C_2} = 2$ ,  $h_\sigma = 3$ , respectively. The class products can be obtained from the multiplication table of the group as explained in § 2.3.

$$\mathcal{C}_E \mathcal{C}_E = \mathcal{C}_E \quad (62)$$

$$\mathcal{C}_{C_2} \mathcal{C}_{C_2} = 2\mathcal{C}_E + \mathcal{C}_{C_2} \quad (63)$$

$$\mathcal{C}_{C_2} \mathcal{C}_\sigma = 2\mathcal{C}_\sigma \quad (64)$$

$$\mathcal{C}_\sigma \mathcal{C}_\sigma = 3\mathcal{C}_E + 3\mathcal{C}_{C_2} \quad (65)$$

The numerical coefficients here are the  $c_{AB,M}$  of Eq. (58). We have seen that  $C_{3v}$  has one two-dimensional representation and two one-dimensional ones. We shall consider the latter. Equation (59) applied to the product  $\mathcal{C}_C \mathcal{C}_C$  of Eq. (63) gives  $2\chi_C \cdot 2\chi_C = 2 + 2\chi_C$ , the solutions of which are  $\chi_C = 1$ ,  $\chi_C = -1/2$ . The latter can be rejected as the characters cannot be fractionary numbers. Hence  $\chi_C = 1$ . With this value, (65) gives  $9\chi_\sigma^2 = 3 + 6$ , hence  $\chi_\sigma = \pm 1$ . As both these alternatives are possible, we shall have two one-dimensional representations, in both of which  $\chi_E = 1$ ,  $\chi_C = 1$  (see Table XX, where they are denoted with the conventional symbols  $A_1$  and  $A_2$  respectively, explained in Table XII, § 6.4).

The characters of the two-dimensional representation will now be obtained. From (63)  $\chi_C^2 = 2 + 2\chi_C$ , which gives  $\chi_C = 2$  or  $\chi_C = -1$ . We therefore find two representations. From (65):  $9\chi_\sigma^2/4 = 3 + 3\chi_C$ . When  $\chi_C = 2$  we have  $\chi_\sigma = \pm 2$ ; when  $\chi_C = -1$  we get  $\chi_\sigma = 0$ . Therefore, we have obtained the following three two-dimensional representations

$E$	$3\sigma$	$2C_3$
2	2	2
2	-2	2
2	0	-1.

We see at once, from the considerations related to the use of Eq. (57) of § 3.9, that the first two representations listed are reducible, as their characters are twice the characters of the one-dimensional representations  $A_1$  and  $A_2$  (see Table XX). The last representation is therefore the only irreducible one, and we list it in Table XX, which gives the characters of all the irreducible representations of  $C_{3v}$ . We denote in the table the two-dimensional representation with the symbol  $E$ , (not to be confused with that for the identity operation), explained in Table XII, § 6.4.

## 4. The Direct Product

### 4.1 Direct Product of Groups

We shall first consider the abstract definition of the direct product. We shall then be able to see, by considering examples of physical interest, that this is a concept of great importance in the application of group theory to quantum mechanics.

Given two groups

$$\begin{aligned} \mathbf{J} &= J_1 + J_2 + \dots + J_p \\ \mathbf{K} &= K_1 + K_2 + \dots + K_q \end{aligned}$$

the elements  $J_t K_u$  ( $t = 1, 2, \dots, p$ ;  $u = 1, 2, \dots, q$ ) form a group  $L$  in the two following cases,

1. when  $J = K$ ,
2. when  $J_t K_u = K_u J_t$  for all  $t$  and  $u$ .

The group  $L$  is called the *direct product* of  $J$  and  $K$  and is denoted with the symbol  $L = J \times K$ . The elements of  $L$  will often be denoted with a double suffix,  $L_{tu} = J_t K_u$ .

The proof that  $L$  forms a group is obvious in the case 1. In the case 2, we prove first that the product of any two elements of  $L$  belongs to  $L$ :  $L_{tu} L_{vw} = J_t K_u J_v K_w = J_t J_v K_u K_w$ . Now  $J_t J_v \in J$ ,  $K_u K_w \in K$  and therefore  $L_{tu} L_{vw}$  is the product of an element of  $J$  by an element of  $K$  and belongs to  $L$ . The existence of the identity element is proved as follows. Call  $J_1$  and  $K_1$  the identity elements of  $J$  and  $K$  respectively. Then  $J_1 K_1 L_{tu} = J_1 K_1 J_t K_u = J_1 J_t K_1 K_u = J_t K_u = L_{tu}$ . Hence, the identity element of  $L$  is the product of those of  $J$  and  $K$ . The existence of the inverse is proved similarly and is left to the reader.

The simplest physical case where the concept of the direct product arises appears when we have two noninteracting systems. These are in fact idealized systems often considered to set up the zero-order wave function in a perturbation calculation — particles at infinite separation, spin and orbital motions, etc. Let us call (1) and (2) two such systems. If we are contemplating a perturbation calculation to make allowance for the weak interactions between them, we are interested in the composite system. If  $H^{(1)}$  and  $H^{(2)}$  are the separate Hamiltonians of the systems 1 and 2 respectively, that of the composite system (interaction neglected) is  $H = H^{(1)} + H^{(2)}$ . Also, the total wave function is  $\psi = \psi^{(1)} \psi^{(2)}$ , where  $\psi^{(1)}$  and  $\psi^{(2)}$  are the wave functions of the systems 1 and 2 respectively. We shall now show that the Schrödinger group  $G$  of the composite system is the direct product of the groups  $G^{(1)}$  and  $G^{(2)}$  of the separate systems. In fact, if we apply any symmetry operation  $G_i^{(1)}$  of  $G^{(1)}$  on the system 1, the wave functions of the system 2 are left undisturbed, because the systems 1 and 2 are not interacting. Therefore  $G_i^{(1)} \psi^{(2)} = \psi^{(2)}$  for all  $i$ , i.e., the operations of  $G^{(1)}$  are all the identity operation with respect to the operands of system 2. Analogously  $G_j^{(2)} \psi^{(1)} = \psi^{(1)}$  for all  $j$ . The operations of the composite system are of the form  $G_i^{(1)} G_j^{(2)}$ , and they operate on the total wave functions  $\psi^{(1)} \psi^{(2)}$ :

$$G_i^{(1)} G_j^{(2)} (\psi^{(1)} \psi^{(2)}) = G_i^{(1)} G_j^{(2)} \psi^{(1)} G_i^{(1)} G_j^{(2)} \psi^{(2)} = G_i^{(1)} \psi^{(1)} G_j^{(2)} \psi^{(2)}. \quad (66)$$

In the first step here we use the fact that  $R/g = R/Rg$  (see § 1.5). In the second step we apply the relations found above, and also the fact that

$G_j^{(2)}\psi^{(2)}$  will always be expressed in terms of the wave functions of system 2, so that  $G_i^{(1)}$  is still the identity with respect to this expression. In exactly the same manner we find that

$$G_j^{(2)}G_i^{(1)}(\psi^{(1)}\psi^{(2)}) = G_i^{(1)}\psi^{(1)}G_j^{(2)}\psi^{(2)}. \quad (67)$$

Comparing (66) and (67) we find that  $G_i^{(1)}G_j^{(2)} = G_j^{(2)}G_i^{(1)}$  for all  $i$  and  $j$ . Hence the operations of the systems 1 and 2 commute in the manner required in the definition of the direct product and we can write  $G = G^{(1)} \times G^{(2)}$ .

The second example of direct product that we shall consider is essentially similar to the case just given, although the similarity is not immediately obvious. Let us consider the group of operations of the triangular prism,  $D_{3h}$  (see § 6.2), which is represented in Fig. 10.

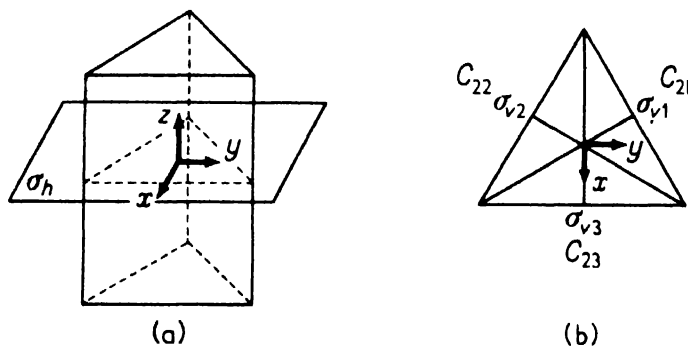


FIG. 10. The operations of the triangular prism ( $D_{3h}$ ). (b) shows the symmetry planes and axes on a section of the prism equidistant from the bases.

The operations of  $D_{3h}$  can be classified in two sets. One is given by the operations that act on the  $xy$ -plane only and leave the  $z$ -axis invariant. These are just the familiar operations of  $C_{3v}$  — identity  $E$ , two threefold rotations around  $z$ , and the three reflections in the lines perpendicular to the sides of the triangular base. These are essentially two-dimensional operations, in the sense that they can be fully defined in a plane, such as the  $xy$  one. The remaining operations, instead, can be considered to arise from the symmetry in the direction of the  $z$ -axis. They are  $\sigma_h$ , (the reflection in a plane perpendicular to the  $z$ -axis), two threefold rotary reflections  $S_6^+, S_6^-$  around the  $z$ -axis, and three binary rotations  $C_2$  around axes perpendicular to the  $z$ -axis.

The symmetry operations of  $D_{3h}$  can be listed as follows:

$$\begin{aligned} E, \quad \sigma_h &= E\sigma_h, \\ C_3^\pm, \quad S_6^\pm &= C_3^\pm\sigma_h, \\ \sigma_{vj}, \quad C_{2j} &= \sigma_{vj}\sigma_h, \quad j = 1, 2, 3. \end{aligned}$$

It is clear, from the considerations given at the end of § 1.4 that  $\sigma_h$  commutes with all the operations of  $C_{3v}$ . Hence, if the group made up of the identity operation and  $\sigma_h$  is called  $C_s$ , we can write

$$D_{3h} = C_{3v} \times C_s$$

A comparison with the example previously given can be easily made if we think of the operands of  $C_{3v}$  as functions of  $x$  and  $y$  only, and those of  $C_s$  as functions of  $z$ . Our previous separate systems are now subspaces of the total configuration space. The lack of interaction between the two subsystems is now replaced by the entirely equivalent requirement that the operators of one subspace leave the other invariant.

The rest of this section will be devoted to obtain the representations of the direct product in terms of those of the component groups.

#### 4.2 The Representation of the Direct Product: Direct Product of Vectors and Matrices

Assume that we possess representations of the groups  $J$  and  $K$  on bases  $\langle j|$  and  $\langle k|$  respectively:

$$Jj_r = \sum_m j_m D(J)_{mr} \quad (68)$$

$$Kk_s = \sum_n k_n D(K)_{ns}. \quad (69)$$

We want to obtain the representations of the direct product  $L = J \times K$  of the two groups. We must first find an appropriate basis for the representation. In the first of the examples given in the last section we saw that the operands of the direct product operators were just products of the operands of each of the component groups. As the functions of the basis must be chosen among the operands of the corresponding groups we must expect an analogous property for the basis. We shall therefore see whether we can use in general the functions  $j_m k_n$  to form the required basis. We must write these functions as a row vector  $\langle l|$  and we choose to do this as follows:

$$\langle l| = \langle j_1 k_1, j_1 k_2, \dots, j_2 k_1, j_2 k_2, \dots | \equiv \langle j_1 | \langle k_1 |, j_2 | \langle k_1 |, \dots |.$$

This is defined as the *direct product* of the two vectors  $\langle j|$  and  $\langle k|$ ,  $\langle l| = \langle j| \times \langle k|$ . It is the vector obtained by replacing the components of the *first* vector by the product of them with the second vector. (Note that  $\langle j| \times \langle k| \neq \langle k| \times \langle j|$ .) The order for the components  $j_m k_n$  is such that the numerical suffixes  $m, n$ , considered as a two-letter "word," are arranged in *dictionary order*. This means that we first take the words with the lowest first "letter" and arrange them in the order in which the second "letter" increases; we then take the words with the second highest first letter and arrange them in the same order, and so on.

The components of the vector  $\langle l|$  can be most advantageously denoted with a double suffix

$$l_{rs} = j_r k_s.$$

The dictionary order of the double suffixes permits us to define a one-dimensional array with them, as is necessary to denote the components of a vector.

A representative  $D(L)$  of  $\mathbf{L}$  will now be defined by the condition

$$Ll_{rs} = \sum_{mn} l_{mn} D(L)_{mn,rs}. \quad (70)$$

Notice here that the double suffix is used just as one unit. It is also clear that the rows and columns of  $D(L)$  will be denoted with double suffixes, arranged of course in dictionary order. We want to obtain  $D(L)_{mn,rs}$  in terms of the matrix elements of  $D(J)$  and  $D(K)$ . In fact, as before,

$$Ll_{rs} = JKj_r k_s = JKj_r JKk_s = Jj_r Kk_s. \quad (71)$$

On introducing (68) and (69) into (71) we obtain

$$Ll_{rs} = \sum_{mn} j_m k_n D(J)_{mr} D(K)_{ns} = \sum_{mn} l_{mn} D(J)_{mr} D(K)_{ns}. \quad (72)$$

Comparison of (70) and (72) gives

$$D(L)_{mn,rs} = D(J)_{mr} D(K)_{ns}. \quad (73)$$

A matrix defined in this manner is called the *direct product* (or *Kronecker product*) of the matrices given, and is denoted with the symbol  $D(L) = D(J) \times D(K)$ . It is formed by substituting every matrix element of the *first* matrix by its product with the whole of the second matrix. As an example, we have, from (73),

$$\begin{array}{c}
 \begin{array}{cc} \mathbf{1} & \mathbf{2} \end{array} \\
 \mathbf{1} \left\| \begin{array}{cc} a_{11} & a_{12} \\ a_{21} & a_{22} \end{array} \right\| \times \begin{array}{c} \mathbf{1} \quad \mathbf{2} \quad \mathbf{3} \\ \left\| \begin{array}{ccc} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{array} \right\| =
 \end{array}
 \end{array}$$
  

$$\begin{array}{ccccc}
 & \mathbf{11} & \mathbf{12} & \mathbf{13} & \mathbf{21} & \mathbf{22} & \mathbf{23} \\
 \begin{array}{c} \mathbf{11} \\ \mathbf{12} \\ \mathbf{13} \\ \mathbf{21} \\ \mathbf{22} \\ \mathbf{23} \end{array} & \left\| \begin{array}{ccc} a_{11}b_{11} & a_{11}b_{12} & a_{11}b_{13} \\ a_{11}b_{21} & a_{11}b_{22} & a_{11}b_{23} \\ a_{11}b_{31} & a_{11}b_{32} & a_{11}b_{33} \\ a_{21}b_{11} & a_{21}b_{12} & a_{21}b_{13} \\ a_{21}b_{21} & a_{21}b_{22} & a_{21}b_{23} \\ a_{21}b_{31} & a_{21}b_{32} & a_{21}b_{33} \end{array} \right\|
 \end{array}$$

The bold figures in the above expression give the numbering of the rows and columns of the matrices.

### 4.3 The Direct Product of Representations

We have shown in the last section that a representation of the direct product of two groups is obtained by forming the direct product of the corresponding matrix representatives of each group (Notice that the expression "direct product" is used here in two different meanings, namely for groups (§ 4.1) and for matrices (§ 4.2).)

We shall now prove the converse theorem, namely that the direct product of two representations is always a representation of the direct product group. To do this we shall require the following identity, which combines the standard and the direct products of matrices.

$$P = (A \times B)(C \times D) = AC \times BD. \quad (74)$$

*Proof.*

$$P_{ij,kl} = \sum_{mn} (A \times B)_{ij,mn} (C \times D)_{mn,kl} \quad (75)$$

$$= \sum_{mn} A_{im} B_{jn} C_{mk} D_{nl} \quad (76)$$

$$= \sum_m A_{im} C_{mk} \sum_n B_{jn} D_{nl} \quad (77)$$

$$= (AC)_{ik} (BD)_{jl} \quad (78)$$

$$= (AC \times BD)_{ij,kl} \quad (79)$$

which proves (74). Here we use in (75) and (78) the ordinary definition of the matrix product and in (76) and (79) that of the direct product of matrices.

To prove the theorem, assume given three groups,  $\mathbf{J}$  and  $\mathbf{K}$  and their direct product  $\mathbf{L} = \mathbf{J} \times \mathbf{K}$ . As shown in § 4.1

$$L_{tu}L_{vw} = L_{xy},$$

where

$$L_{tu} = J_t K_u,$$

$$L_{vw} = J_v K_w,$$

$$L_{xy} = J_x K_y, (J_x = J_t J_v, K_y = K_u K_w).$$

The representations of  $\mathbf{L}$  must satisfy the condition

$$D(L_{tu})D(L_{vw}) = D(L_{xy}). \quad (80)$$

We want to prove that this is the case when

$$D(L_{mn}) = D^i(J_m) \times D^j(K_n). \quad (81)$$

In fact,

$$D(L_{tu})D(L_{vw}) = (D^i(J_t) \times D^j(K_u))(D^i(J_v) \times D^j(K_w)).$$

On applying the equality (74) we obtain

$$D(L_{tu})D(L_{vw}) = D^i(J_t)D^i(J_v) \times D^j(K_u)D^j(K_w),$$

and from the definition of  $J_x$  and  $K_y$ ,

$$D(L_{tu})D(L_{vw}) = D^i(J_x) \times D^j(K_y).$$

From (81) the right-hand side of this expression is  $D(L_{xy})$  which verifies the condition (80). This demonstrates the theorem.

The proof above is valid in particular when  $\mathbf{J}$  and  $\mathbf{K}$  are the same group. It then shows that *the direct product of any two representations of a given group is also a representation of the same group*. (Remember that the direct product of a group by itself is just the same group.) This provides a second method to combine two representations of a group to get a third one, the other method being that of forming the direct sum of the two representations (see § 3.1). -

When  $\mathbf{J}$  and  $\mathbf{K}$  are different groups it can further be proved that: (1) If  $D^i(J)$  and  $D^j(K)$  are irreducible representations of  $\mathbf{J}$  and  $\mathbf{K}$  respectively,  $D(L) = D^i(J) \times D^j(K)$  is also an irreducible representation of  $\mathbf{L} = \mathbf{J} \times \mathbf{K}$ . (2). All the irreducible representations of  $\mathbf{L}$  are given by (81) if  $i$  and  $j$  are varied over all the irreducible representations of  $\mathbf{J}$  and  $\mathbf{K}$ . We leave the proof of these facts to the reader (see also Wigner,<sup>1</sup> Chapter X).



## 4.4 The Characters of the Direct Product Representation

The characters of the representations of the direct products of two groups are just the product of the characters of the representations of the component groups. In fact, for a direct product representation that satisfies (73) we have

$$\chi(L) = \sum D(L)_{rs,rs} = \sum D'(J)_{rr} D'(K)_{ss} = \chi'(J) \chi'(K). \quad (82)$$

We shall show in a first example of the use of this expression how it simplifies the calculation of character tables. Let us consider  $D_{3h} = C_{3v} \times C_s$ . The character table of  $C_{3v}$  was obtained in § 3.10 (see table XX). That of  $C_s$  can be obtained in the same manner, but as  $C_s = E + \sigma_h$  has only two classes and hence two one-dimensional irreducible representations, these can be immediately seen to be those given in Table VII. It is enough, for instance, to apply the orthogonality condition. (See Table XII, § 6.4 for the nomenclature for the irreducible representations used in the first column of Table VII and further below.)

TABLE VII  
CHARACTER TABLE FOR THE GROUP  $C_s$

$C_s$	$E$	$\sigma_h$
$A'$	1	1
$A''$	1	-1

TABLE VIII  
THE CHARACTER TABLE OF  $D_{3h}$  IN RELATION TO THAT OF  $C_{3v}$

$C_{3v}$	$E$	$3\sigma_v$	$2C_3$	$D_{3h}$	$E$	$3\sigma_v$	$2C_3$	$\sigma_h$	$3C_2 = 3\sigma_v\sigma_h$	$2S_6 = 2C_3\sigma_h$
$A_1$	1	1	1	$A_1'$	1	1	1	1	1	1
				$A_1''$	1	1	1	-1	-1	-1
$A_2$	1	-1	1	$A_2'$	1	-1	1	1	-1	1
				$A_2''$	1	-1	1	-1	1	-1
$E$	2	0	-1	$E'$	2	0	-1	2	0	-1
				$E''$	2	0	-1	-2	0	1
			$A_2' \times$	$A_2''$	1	1	1	-1	-1	-1
			$E' \times$	$E''$	4	0	1	-4	0	-1

From the character table of  $C_3$  and Eq. (82) it can be seen at once that each representation of  $C_{3v}$  splits into two of  $D_{3h}$ , as it can be combined with either of the two representations of  $C_3$ . The results are shown in Table VIII.

As a second example we apply (82) for the case  $J = K$ , i.e., for the direct product of two representations of the same group. We give in the last two lines of Table VIII the characters of  $A'_2 \times A'_2$  and those of  $E' \times E''$ . It can be noticed from the table that the characters of  $A'_2 \times A'_2$  coincide with those of  $A''_1$ . Hence the representation  $A'_2 \times A'_2$  must be equal to  $A''_1$ , except perhaps for a unitary transformation. We express this result by writing  $A'_2 \times A'_2 = A''_1$ . On the other hand the representation given by  $E' \times E''$  is clearly a reducible one and the number of times that each irreducible representation appears in it can be obtained from Eq. (57) of § 3.9 or by inspection (looking for linear combinations of the characters of the irreducible representations that add up to those of the reducible one). We obtain

$$E' \times E'' = A''_1 + A'_2 + E'', \quad (83)$$

which means that the representations listed in the right appear once each in the reducible one of the left. The plus sign in (83) must be understood in the sense of a direct sum

Direct products may have more than two factors. It is simple for instance to find the characters of  $E' \times E'' \times A'_2$  and by the same procedure used above we obtain

$$E' \times E'' \times A'_2 = A'_1 + A'_2 + E'. \quad (84)$$

Relations such as (83) and (84) will be found important later on (see § 5.6). Also the following theorem:

*The direct product of two representations contains the totally symmetrical one if and only if the representations are conjugate.* Here the totally symmetrical representation is that for which all its characters  $\chi^i(\mathcal{C})$  are equal to unity and two representations are called conjugate when for all the classes  $\chi^i(\mathcal{C}) = \chi^j(\mathcal{C})^*$ . The number of times  $a^{(s)}$  that the totally symmetrical representation is contained in the direct product of the representations  $i$  and  $j$  is given by

$$\begin{aligned} a^{(s)} &= \frac{l}{h} \sum_{\mathcal{C}} h_{\mathcal{C}} \chi^i(\mathcal{C})^* \chi^j(\mathcal{C}) \chi^s(\mathcal{C}) \\ &= \frac{l}{h} \sum_{\mathcal{C}} h_{\mathcal{C}} \chi^i(\mathcal{C})^* \chi^j(\mathcal{C}) = 1, \end{aligned}$$

(see (57), § 3.9). The last equality, which results from (53), § 3.9, shows that the condition that the representations be conjugate is a sufficient one for the direct product to contain the totally symmetrical representation. It is easy to prove, from the orthogonality of the characters, that it is also a necessary condition, but we leave this to the reader.

## 5. Symmetry Properties of Functions

### 5.1 Symmetry Adapted Functions

Given a function  $\varphi_s^{(i)}$  of a basis that spans the  $i$ th irreducible representation of a group  $G$ , we know that for all  $R \in G$

$$R\varphi_s^{(i)} = \sum_r \varphi_r^{(i)} D^i(R)_{rs}. \quad (85)$$

We shall say that the function  $\varphi_s^{(i)}$  is transformed by or belongs to the  $s$ th column of the  $i$ th irreducible representation.\* A function with this type of symmetry behaviour will be called a *symmetry adapted function*.†

Our main problem in this section will be first, to generate symmetry adapted functions starting from arbitrary ones, and secondly, to expand arbitrary functions in terms of symmetry adapted functions. Both problems have already been solved in principle in § 3.3, but we shall give here a simple technique to achieve the desired results.

It should first be noticed that Eq. (85) is not a practical one to check whether a given function belongs or not to a given column of a representation. This is so because the use of (85) involves the knowledge of all the functions  $\varphi_r^{(i)}$  of the basis ( $r = 1, 2, \dots, l_i$ ,  $l_i$  being the dimension of the representation) which we shall call the *partners* of  $\varphi_s^{(i)}$ . We shall derive from (85) an expression that is free from this restriction.

On multiplying both sides of (85) by  $D^i(R)_{tu}^*$  and adding over all  $R$  in  $G$  we obtain

$$\sum_R D^i(R)_{tu}^* R\varphi_s^{(i)} = \sum_r \varphi_r^{(i)} \sum_R D^i(R)_{tu}^* D^i(R)_{rs},$$

which, on using the orthogonality condition (42), gives

$$\sum_R D^i(R)_{tu}^* R\varphi_s^{(i)} = \sum_r \varphi_r^{(i)} \frac{h}{l_i} \delta_{ti} \delta_{rt} \delta_{su} = \varphi_t^{(i)} \frac{h}{l_i} \delta_{ti} \delta_{su}. \quad (86)$$

\* Notice that this terminology differs from that used by Wigner.<sup>1</sup>

† An expression coined by Melvin.<sup>22</sup>

Hence, we obtain

$$\sum_{\mathbf{R}} D^i(\mathbf{R})_{is}^* \mathbf{R} \varphi_s^{(i)} = \frac{\hbar}{l_i} \varphi_t^{(i)}, \quad t = 1, 2, \dots, l_i. \quad (87)$$

We take the particular case  $t = s$  in (87), so as to have an expression that contains the function  $\varphi_s^{(i)}$  only:

$$\sum_{\mathbf{R}} D^i(\mathbf{R})_{ss}^* \mathbf{R} \varphi_s^{(i)} = \frac{\hbar}{l_i} \varphi_s^{(i)}. \quad (88)$$

This is a convenient formula to test the symmetry properties of a given function.

## 5.2 Formation of a Symmetry Adapted Function

We shall now consider the following problem: given an arbitrary function  $\phi$ , to obtain from it a function that belongs to the  $t$ th column of the  $i$ th irreducible representation of a group. This is for instance what we did in a one-dimensional space when we derived from an arbitrary function  $f(x)$  the even combination  $f(x) + f(-x)$ .

Let us consider Eq (87) for this purpose. We see from it that the operator

$$\sum_{\mathbf{R}} D^i(\mathbf{R})_{it}^* \mathbf{R}$$

applied on a function that belongs to the  $s$ th column of the  $i$ th irreducible representation transforms it into a function that belongs to the  $t$ th column of the same representation. We shall see however that this operator is much more powerful, as it produces a symmetry adapted function of the type mentioned when acting on any arbitrary function  $\phi$ . Moreover, this is the case for any value of the suffix  $s$  ( $s = 1, 2, \dots, l_i$ ). Let us define a *symmetrizing operator*  $\mathbf{W}_{is}^i$  as follows

$$\mathbf{W}_{is}^i \equiv \frac{l_i}{\hbar} \sum_{\mathbf{R}} D^i(\mathbf{R})_{is}^* \mathbf{R}. \quad (89)$$

We want to prove that

$$\mathbf{W}_{is}^i \phi = \frac{l_i}{\hbar} \sum_{\mathbf{R}} D^i(\mathbf{R})_{is}^* \mathbf{R} \phi = \varphi_t^{(i)} \quad (90)$$

is a symmetry adapted function that satisfies Eq. (85), that is,

$$\mathbf{R}_k \varphi_t^{(i)} = \sum_u \varphi_u^{(i)} D^i(\mathbf{R}_k)_{ut}, \quad (91)$$

where  $R_k \in G$  and the functions  $\varphi_u^{(i)}$ , partners of  $\varphi_i^{(i)}$  in the basis, are given by a formula analogous to (90), that is,  $\varphi_u^{(i)} \equiv W_{us}^{(i)} \phi$

On using the definition of  $\varphi_i^{(i)}$  given by (90) the left-hand side of (91) can be written as follows

$$R_k \varphi_i^{(i)} = \frac{l_i}{h} \sum D^i(R)_{is}^* R_k R \phi, \quad (92)$$

where we use the fact that the operators  $R$  are linear. On the other hand, we can put  $D_i(R)_{is}^*$  in the form

$$D^i(R)_{is}^* = D^i(R_k^{-1} R_k R)_{is}^* = \sum D^i(R_k^{-1})_{iu}^* D^i(R_k R)_{us}^*$$

We have seen that  $D(R^{-1}) = D(R)^{-1}$ . Also, as  $D(R)$  is unitary,  $D(R)^{-1} = D(R)^\dagger \equiv \overline{D(R)}^*$ . Therefore  $D^i(R_k^{-1})_{iu}^* = D^i(R_k)_{ui}$ , hence

$$D^i(R)_{is}^* = \sum D^i(R_k)_{ui} D^i(R_k R)_{us}^*$$

On introducing this expression in (92) we have

$$R_k \varphi_i^{(i)} = \sum \left[ \frac{l_i}{h} \sum D^i(R_k R)_{us}^* R_k R \phi \right] D^i(R_k)_{ui} \quad (93)$$

$$\sum \left[ \frac{l_i}{h} \sum D^i(R)_{us}^* R \phi \right] D^i(R_k)_{ui} \quad (94)$$

In the last step we use the fact that when we take all  $R \in G$ ,  $R$  and  $R_k R$  define the same set, namely, the one formed by all the operations of the group  $G$ . The term in the square bracket in (94) is just  $W_{us}^{(i)} \phi \equiv \varphi_u^{(i)}$  so that (94) coincides with Eq (91), which proves the property under consideration

### 5.3 The Projection Operators and the Expansion of a Function in Symmetry Adapted Functions

We can write Eq (86) as follows

$$W_{iu}^{(i)} \varphi_s^{(i)} = \varphi_i^{(i)} \delta_{i, i'} \delta_{s, s'} \quad (95)$$

This equation expresses the fact that when the operator  $W_{iu}^{(i)}$  is applied on symmetry adapted functions,  $\varphi_u^{(i)}$  is the only one that is not annihilated, and it is transformed into  $\varphi_i^{(i)}$ .

To consider the way in which the symmetrizing operators are compounded notice that, in (95), we can write  $\varphi_s^{(i)} = W'_{sr}\phi$  and  $\varphi_i^{(j)} = W'_{id}\phi$ , where  $\phi$  is an arbitrary function. Therefore

$$W'_{iu}W'_{sr}\phi = \delta_{i,} \delta_{su} W'_{id}\phi, \quad (96)$$

so that

$$W'_{iu}W'_{sr} = W'_{id} \delta_{i,} \delta_{su}. \quad (97)$$

Here  $d = 1, 2, \dots, l$ . This expression is the law of composition of the symmetrizing operators and it shows that they are orthogonal. It also indicates the advantage of using those operators for which the two suffixes are identical, such as  $W'_{ii}$ , because these are also idempotent. In fact, from (97)

$$W'_{ii}W'_{ss} = W'_{ii} \delta_{i,} \delta_{si}, \quad (98)$$

so that

$$W'_{ii}W'_{ii} = (W'_{ii})^2 = W'_{ii}, \quad (99)$$

and this is the condition that defines an *idempotent operator* (in general, a Hermitian operator  $R$  is idempotent if  $R^2 = R$ ). Also, from Eq. (95), these operators satisfy the condition

$$W'_{ii}\varphi_s^{(i)} = \varphi_i^{(j)} \delta_{i,} \delta_{si}. \quad (100)$$

This shows that  $W'_{ii}$  leaves invariant the function  $\varphi_i^{(j)}$  and annihilates every other symmetry adapted function, so that it is an operator with eigenvalues 1 (corresponding to  $\varphi_i^{(j)}$ ) and 0 (corresponding to  $\varphi_s^{(i)}$ ,  $s \neq i$  or  $i \neq j$ ) only. It should now be clear that the behaviour of the operators  $W'_{ii}$  is much simpler than that of the  $W'_{iu}$ . In fact, they are analogous to geometrical projections, because when a system of orthogonal unit vectors  $u_s$  ( $s = 1, 2, \dots, n$ ) is projected on one of them,  $u_i$ , all the vectors are annihilated except  $u_i$ , which is left invariant. It can easily be seen that this behaviour is a consequence of the idempotency condition, which explains why it is customary to refer to idempotent operators as *projection operators*.

When  $W'_{ii}$  is applied on an arbitrary function  $\phi$ , the function  $\varphi_i^{(j)}$  is obtained, and this can be considered as one of the components of  $\phi$  in the representation space. When  $j$  varies over all the irreducible representations of the group and  $i$  takes in each case all the values compatible with the dimension of the representation, a basis  $\langle \varphi_i^{(j)} |$  is obtained that spans a completely reduced representation of the group.

The projection operators  $W'_u$  permit us to expand an arbitrary function in terms of functions of the possible symmetry types (symmetry adapted functions) of the group. We have shown in fact (§ 3.3) that it is always possible to write an arbitrary function  $\phi$  as a sum of symmetry adapted functions:

$$\phi = \sum \phi_i^{(j)}. \quad (101)$$

This expansion is formally similar to that of a vector in its components. To make this expansion practicable we must of course be able to find these components. If we operate on both sides of (101) with  $W'_u$ , and apply Eq. (100), we have

$$W'_u \phi = \phi_i^{(j)} \quad (102)$$

so that we can write

$$\phi = \sum W'_u \phi, \quad (103)$$

which is the desired expansion. This shows also that the operators  $W'_u$  form a complete set, so that

$$\sum W'_u = 1. \quad (104)$$

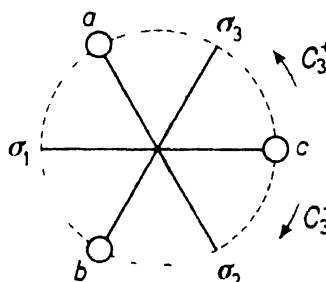


FIG. 11 A triangular molecule

## 5.4 An Example

We shall consider as an example a triangular molecule, say  $H_3$  (see Fig. 11). The symmetry group of this molecule is  $D_{3h}$ . Suppose that the hydrogen atoms are in their ground states (1s) and call  $a$ ,  $b$ ,  $c$  respectively their wave functions. The functions 1s are invariant under the operation  $\sigma_h$ . Also, we have seen that  $D_{3h} = C_{3v} \times C_s$  ( $C_s = E + \sigma_h$ ). As  $\sigma_h$  can be taken to be the identity with respect to the functions considered, all the results will be the same if  $C_{3v}$  rather than  $D_{3h}$  is employed.

We shall take  $a$  as the arbitrary function from which to obtain symmetry adapted ones. As the symmetrizing operators involve the transforms of  $a$  under all the operations of the group, we list them in the first column of Table IX. In the successive columns we list the matrix elements of the irreducible representations of the group, as obtained from Table IV (re-

presentations  $A_1$  and  $E$ ) and Table XX (representation  $A_2$ ). These will be used in forming the operators  $W'_{sr}$ .

TABLE IX  
DATA TO FORM PROJECTION OPERATORS FOR THE GROUP  $C_{3v}$

R	Ra	$D^{A_1}(R)_{11}^*$	$D^{A_2}(R)_{11}^*$	$D^E(R)_{11}^*$	$D^E(R)_{12}^*$	$D^E(R)_{21}^*$	$D^E(R)_{22}^*$
E	a	1	1	1	0	0	1
$\sigma_1$	b	1	-1	1	0	0	-1
$\sigma_2$	a	1	-1	$-\frac{1}{2}$	$-\frac{\sqrt{3}}{2}$	$-\frac{\sqrt{3}}{2}$	$\frac{1}{2}$
$\sigma_3$	c	1	-1	$-\frac{1}{2}$	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$	$\frac{1}{2}$
$C_3^+$	c	1	1	$-\frac{1}{2}$	$-\frac{\sqrt{3}}{2}$	$-\frac{\sqrt{3}}{2}$	$-\frac{1}{2}$
$C_3^-$	b	1	1	$-\frac{1}{2}$	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$	$-\frac{1}{2}$

The operators  $W'_{sr}$  are obtained at once from the table

$$W_{11}^{A_1}a = \frac{1}{6}(a + b + a + c + c + b) = \frac{1}{3}(a + b + c) \quad (105)$$

$$W_{11}^{A_2}a = \frac{1}{6}(a - b - a - c + c + b) = 0 \quad (106)$$

$$W_{11}^Ea = \frac{2}{6}(a + b - \frac{1}{2}a - \frac{1}{2}c - \frac{1}{2}c - \frac{1}{2}b) = \frac{1}{3}(\frac{1}{2}a + \frac{1}{2}b - c) \quad (107)$$

$$W_{12}^Ea = \frac{1}{3}\frac{\sqrt{3}}{2}(2c - a - b) \quad (108)$$

$$W_{21}^Ea = \frac{1}{3}\frac{\sqrt{3}}{2}(b - a) \quad (109)$$

$$W_{22}^Ea = \frac{1}{3}\frac{2}{3}(a - b) \quad (110)$$

It results from (107) and (108) that  $W_{12}^Ea = -\sqrt{3}W_{11}^Ea$ , also from (109) and (110) that  $W_{21}^Ea = -\frac{1}{3}\sqrt{3}W_{22}^Ea$ . This is as expected, on account of the nature of the second suffix of the symmetrizing operators. (The constant factors, of course, do not affect the symmetry of the functions. They cannot be expected to be the same for the symmetrizing and projection operators, as for the former the expansion (103) is not valid.) The results



obtained with the projection operators (cf. 105, 107 and 110 are summarized below.

$$\begin{aligned}a^{A_1} &= \frac{1}{3}(a + b + c) \\a_1^E &= \frac{1}{3}(2c - a - b) \\a_2^E &= \frac{1}{2}(a - b).\end{aligned}\tag{111}$$

We see that

$$a^{A_1} + a_1^E + a_2^E = a \tag{112}$$

as expected, because this equation is the expansion of  $a$  in its components or symmetry adapted functions (cf. 101).

It should be noted that the numerical coefficients in (111) have been kept only to obtain the correct check in (112). In practice, an expression like the latter is very seldom needed, whereas the interest is centred in the symmetry adapted functions. Hence, the numerical coefficients of the latter are irrelevant and in fact they are usually replaced by appropriate normalization coefficients.

The method used in the treatment of this example can also be considered as a general one to reduce a representation. In fact, the functions  $a^{A_1}$ ,  $a_1^E$ ,  $a_2^E$  can be readily seen to span a representation identical with the one given in Table III of § 1.7. By using the method given in § 3.9 (formula 57), and the character table of  $C_{3v}$ , it can be seen that this representation must reduce into  $A_1 + E$ . The functions given in (111), in fact, span this reduced representation and this explains why the "component" of  $a$  in the  $A_2$  irreducible representation turned out to be null

### 5.5 Functions That Belong to a Representation

The use of the operators  $W_j'$  requires a complete knowledge of the irreducible representation  $j$ . As these are not as easily accessible as the character tables, the technique discussed in the present section is most often used.

We shall say that a function  $\phi'$  belongs to the  $j$ th irreducible representation of a group  $G$  if it is given by a linear combination of all the symmetry adapted functions of this representation of the form

$$\phi' = \sum c_i' \phi_i, \tag{113}$$

where the  $c_r^j$  are arbitrary coefficients. Expression (113) can be written as follows, in terms of any given function  $\phi$ ,

$$\phi' = \sum_r W_{rr}' \phi \equiv V^j \phi, \quad (114)$$

where we have introduced the operator\*

$$V^j \equiv \sum_r W_{rr}'.$$

This can be given explicitly, on introducing the definition of the projection operator,

$$V^j = \frac{l_j}{h} \sum_R \left[ \sum_r D^j(R)_{rr}^* \right] R = \frac{l_j}{h} \sum_R \chi^j(R) R. \quad (115)$$

In the last step we use the definition of the character. A function  $\phi^j$  that belongs to the representation  $j$  is given by

$$\phi^j = V^j \phi = \frac{l_j}{h} \sum_R \chi^j(R) R \phi. \quad (116)$$

As an example of the use of these operators we shall consider the one given in § 5.4. We give in the first three columns of Table X the transforms of the functions  $a$ ,  $b$  and  $c$  defined in § 5.4, and in the following ones the characters of the representations of  $C_{3v}$ .

TABLE X  
DATA TO FORM THE OPERATORS  $V^j$  FOR  $C_{3v}$

R	Ra	Rb	Rc	$\chi^{A_1}$	$\chi^{A_2}$	$\chi^E$
E	a	b	c	1	1	2
$\sigma_1$	b	a	c	1	-1	0
$\sigma_2$	a	c	b			
$\sigma_3$	c	b	a			
$C_3^+$	c	a	b	1	1	-1
$C_3^-$	b	c	a			

\* It should be noticed that in (114) we have dropped the coefficients  $c_r^j$  because, as explained in § 5.4, they can be included in the arbitrary coefficients implicit in the combinations  $W_{rr}' \phi$ .

We list in Table X the transforms of all the functions of the set given under all the operations of the group because if we take only one function in the place of  $\phi$  in Eq. (116) we shall get only one function that belongs to the representation considered. If this latter is degenerate, we must obtain more than one function  $\phi'$  belonging to it, so as to be able to derive from them the right number of independent symmetry adapted functions  $\phi'_i$ . Therefore, we must use (116) for a number of the functions of the set given equal at least to the dimension of the representation.

We find, dispensing now with the numerical coefficients of the combinations,

$$a^{A_1} = a + b + c \quad (117)$$

$$a^{A_2} = 0 \quad (118)$$

$$a^E = 2a - b - c \quad (119)$$

$$b^E = 2b - a - c \quad (120)$$

$$c^E = 2c - a - b \quad (121)$$

The first two results agree with those found in § 5.4 (see 111). On the other hand, we get three, rather than two functions that belong to  $E$ . It is clear that the method used here does not guarantee the linear independence of the functions obtained, and in fact  $a^E + b^E + c^E = 0$ , so that they are not linearly independent. Therefore, we could strike out any one of the three functions (119), (120), and (121), and use the remaining two only. Often, however, as is the case here, we can do better. On account of the definition of  $a^E$ ,  $b^E$  and  $c^E$ , linear combinations of them that belong to different columns of the irreducible representation  $E$  could, in principle, be formed. We shall see how this can be done without using the full representation of  $C_{3v}$ .

As the three reflections  $\sigma_1$ ,  $\sigma_2$ ,  $\sigma_3$ , do not commute we cannot reduce simultaneously the three matrix representatives to diagonal form. However, any one of them can be independently diagonalized. As the diagonal matrix obtained must be unitary and of null trace ( $\chi(\sigma) = 0$ ) it must be

$$\begin{vmatrix} 1 & \\ & -1 \end{vmatrix}.$$

With reference to the basis of the representation, this means that one of the functions of it will be symmetrical, and the other antisymmetrical with respect to the particular reflection considered. This can be any one of the

operations in the class and we take it to be  $\sigma_1$ .<sup>\*</sup> We notice that (121) is already symmetrical with respect to  $\sigma_1$ , so that it must be our  $a_1^E$ . The antisymmetric combination of (119) and (120) is  $a^E - b^E = 3(a - b)$ . This must be our  $a_2^E$ . The results can be seen to agree with those of last section, except of course for a numerical factor.

### 5.6 Orthogonality Properties of Functions

We shall prove that two functions that belong to different irreducible representations or to different columns of the same one are orthogonal. As before, we shall use the notation  $(f, g) = \int f^* g d\tau$ . Because of the unitary character of the operators  $R$ , we have  $(\phi_s^{(i)}, \phi_t^{(j)}) = (R\phi_s^{(i)}, R\phi_t^{(j)})$ , so that

$$\begin{aligned} (\phi_s^{(i)}, \phi_t^{(j)}) &= \left( \sum_m \phi_m^{(i)} D^i(R)_{ms}, \sum_n \phi_n^{(j)} D^j(R)_{nt} \right) \\ &= \sum_{mn} D^i(R)_{ms}^* D^j(R)_{nt} (\phi_m^{(i)}, \phi_n^{(j)}) \end{aligned} \quad (122)$$

We now sum both sides of (122) over all the operations  $R$  of the group  $G$  (order  $h$ ) and apply the orthogonality conditions for the matrix elements of the irreducible representations. We then obtain

$$h(\phi_s^{(i)}, \phi_t^{(j)}) = \frac{h}{\sqrt{l_i l_j}} \delta_{ij} \delta_{st} \sum_n (\phi_n^{(i)}, \phi_n^{(j)})$$

As the right-hand side of this expression vanishes if either  $i \neq j$  or  $s \neq t$ , the theorem is proved.

It is instructive to obtain this important result in a different way. Consider an integral

$$= \int f(q) dq \quad (123)$$

where the variables  $q$  are defined in a multidimensional space  $\Omega$  of given symmetry  $G$ . The operations  $R$  of  $G$  are covering operations of this space.

<sup>\*</sup> We get agreement in this way with the results obtained by the more detailed method of § 5.4 but, had  $\sigma_2$ , say, been the chosen reflection, the results obtained would have been equally correct, although different from those of last section, as they would correspond to a representation equivalent to but not identical with that used in it.

We can always change variable in (123) without changing the value of the integral, and we shall do so by applying the operation  $R^{-1} \in \mathbb{G}$  on the variable  $q$ .

$$I = \int_{R^{-1}\Omega} f(R^{-1}q) d(R^{-1}q). \quad (124)$$

We have (cf. Eq. 13, § 1.5)  $d(R^{-1}q) = R dq$  and, as it is the same thing to apply an operation  $R$  on the differential or the operation  $R$  on the volume of integration we can write

$$I = \int_{RR^{-1}\Omega} f(R^{-1}q) dq = \int_{\Omega} f(R^{-1}q) dq = \int_{\Omega} Rf(q) dq. \quad (125)$$

The function  $f(q)$  can always be expressed as a linear combination of functions  $f_i^{(j)}(q)$  that belong to the  $i$ th column of the  $j$ th irreducible representation of  $\mathbb{G}$ . Correspondingly  $I$ , as given by (125) will split up into terms that we can denote with  $I_i^{(j)}$ , each containing  $Rf_i^{(j)}(q)$  in the integrand. On writing

$$Rf_i^{(j)}(q) = \sum_s f_s^{(j)}(q) D^j(R)_{st}$$

we have

$$I_i^{(j)} = \sum D^j(R)_{st} \int f_s^{(j)}(q) dq. \quad (126)$$

We now add up over all the elements of the group. The left-hand side of (126) is multiplied by  $h$ , the order of the group, and we obtain

$$hI_i^{(j)} = \sum \left( \sum D^j(R)_{st} \right) \int f_s^{(j)}(q) dq. \quad (127)$$

Unless  $j$  denotes the totally symmetrical representation the summation over  $R$  in (127) vanishes, as follows from the orthogonality condition (49) when all the matrix elements  $D^j(R)$  are taken as equal to the unity, which is the case when they correspond to the totally symmetrical representation. It is clear from (127) that the only term  $I_i^{(j)}$  different from zero will be that in which  $j$  corresponds to the totally symmetrical representation.

We have therefore shown that the necessary and sufficient condition for an integral such as (123) to be different from zero is that the representation generated by its integrand contains the totally symmetrical representation.

It is quite clear that this result agrees with the criterion given at the beginning of this section for integrals of the type  $\int f^* g \, d\tau$ , because we have seen (§ 4.4) that the necessary and sufficient condition for the direct product of the representations spanned by  $f^*$  and  $g$  to contain the totally symmetrical representation is that  $f^*$  and  $g$  belong to conjugate representations (and hence  $f$  and  $g$  to the same one).

The rules given in this section have many important consequences. Our first example will be concerned with transition selection rules. Consider a transition probability integral in a system with symmetry  $D_{3h}$ , of the form  $I = \int \psi^{E'} \mathbf{z} \psi^{E''} \, d\tau$ , where the superscripts denote the representation to which the wave function belongs. It can be seen (cf. § 6.5 and Table XXIII) that  $\mathbf{z}$  belongs to the representation  $A_2''$  of  $D_{3h}$ , so that in order to find the symmetry of the integrand we must form the direct product  $E' \times E'' \times A_2''$ . This (cf. Eq. 84, § 4.4) contains the totally symmetrical representation  $A_1'$  so that  $I \neq 0$ .

Sometimes it is desirable to consider the above problem in a slightly more general form. We have an integral such as  $\int \psi^{E'} \mathbf{a} \psi^{E''} \, d\tau$ , where  $\mathbf{a}$  is  $\mathbf{x}$ ,  $\mathbf{y}$ , or  $\mathbf{z}$ , and we want to determine for which of these vectors it is different from zero. We form the direct product  $E' \times E'' = A_1'' + A_2'' + E''$  (cf. Eq. 83). We must now find a vector  $\mathbf{x}$ ,  $\mathbf{y}$  or  $\mathbf{z}$  that belongs to either of the three last mentioned representations (if this is the case its direct product by  $E' \times E''$  will contain the totally symmetrical representation since  $E' \times E''$  and the vector considered will have one representation in common, see § 4.4). We see from Table XXIII that  $\mathbf{z} \in A_2''$  and  $\mathbf{x}, \mathbf{y} \in E'$ , so that the integral with  $\mathbf{a} = \mathbf{z}$  is the only one that does not vanish.

An example of much practical importance is the *factorization of secular determinants*. The matrix elements of these are of the form  $\int f^* H g \, d\tau$ . As the Hamiltonian belongs always to the totally symmetrical representation of the group of the Schrödinger equation (this is in fact the definition of this group) it will never alter the symmetry of the direct product of  $f^*$  by  $g$ , and hence it is enough to consider these functions only; that is, the matrix elements will be different from zero only when  $f$  and  $g$  belong to the same column of the same irreducible representation. To take full advantage of this fact it is convenient, before setting up the secular determinant, to transform the original functions into symmetry adapted ones, by the methods given before. If we obtain only functions that belong to the various irreducible representations of the group, the secular determinant will be made up of diagonal blocks, each one corresponding to one representation. These blocks will have the dimension of the corresponding representation. If we go further and obtain functions belonging to the individual columns of

the irreducible representations, the secular determinant will be fully diagonalized, unless a particular representation appears more than once in it.

## 6. Some Important Groups

We shall discuss in this section the properties of the groups that are of more importance in physical applications. These, as already mentioned in § 3.4, are the point groups and the permutation groups.

The *point groups*, of which we have considered a number of examples in this chapter, arise in systems of points that have certain symmetry elements. The corresponding symmetry operations are such that they cover the set of points into itself, and it is clear that they form a group. These groups appear mainly in the study of molecules and, as we have seen, the corresponding group theory permits us to classify the energy levels in them.

The point groups are essentially *rotation groups*\* in the sense that the operations of them are either simple rotations (also called *proper rotations*) or products of them by the inversion operation (as in the case of reflections, see § 1.3). They are also important in crystals, although here they are only a part of the whole group of the covering operations of the system, which is called a *space group*. In fact, if the crystal is supposed to be an infinite one, *translations* (i.e., operations that add a constant to the coordinates of every point of the space) appear as covering operations of it. The translations form a subgroup,<sup>†</sup> as the product of any two translations is also a translation. It is also easy to understand that the conjugate of a translation must also be a translation. The reason behind this result<sup>‡</sup> is that one cannot

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\* Rotations are operations that leave just one point (or an axis) of a body invariant. If the rotation angle can take any value, as for instance in the rotation around the axis of a cylinder, the group is a *continuous* one, i.e., a group of infinite order the elements of which can be numbered with a continuous parameter. We are concerned here with subgroups of the infinite rotation group, namely those for which the rotation angles can take finite values only.

<sup>†</sup> This is one of infinite order, which would make its treatment very difficult. On the other hand, if the crystal is supposed to be finite, the translation operations cease to be symmetry operations of the lattice. To circumvent this difficulty the lattice is conceived as infinite (so that translations are symmetry operations), through a periodic repetition of the finite volume of the real crystal. The periodicity means that when the whole of the crystal occupies the second period, its position is identical with that it had in the first period. The particular translation that effects this result becomes then equal to the identity operation and it can be readily seen that the translation group becomes a finite one, and in fact cyclic (or rather, the direct product of cyclic groups). This useful procedure was introduced by Born and von Kármán.

<sup>‡</sup> See Burckhardt<sup>16</sup> for a rigorous discussion, as well as for the detailed theory of space groups.

expect a change in the coordinates system to transform a translation operation into a rotation (cf. the meaning of conjugate operations explained in § 2.3). Hence the translation group is an invariant subgroup of the space group. We shall only give the main results of the theory of the space groups. Not all possible point groups are such that they can leave a translation group invariant: the only rotation axes permitted are binary, ternary, four- and sixfold. (Regular pentagons, for instance, cannot be joined together into a lattice.) It then follows that the point groups that can be appropriately combined with translation groups are no more than 32. These are called the *crystallographic point groups*. Also, there are only fourteen different types of translation groups, which are called the *Bravais lattices*. By combining each of them with all the point groups that are compatible with a given lattice, 230 space groups can be formed in three dimensions.

The *permutation groups* appear in the treatment of many-particle systems and as such are of great importance in atomic and nuclear physics. To write down the Hamiltonian of a system of  $n$  identical particles, we must first label them  $1, 2, 3, \dots, n$ . Let us denote the corresponding expression of the Hamiltonian with  $H(1, 2, \dots, n)$ . As the particles are identical, we can relabel them in a different order, such as  $2, 1, 3, \dots, n$ , and this will not introduce any changes in the observable quantities of the system, and therefore neither in the Hamiltonian  $H(1, 2, 3, \dots, n) = H(2, 1, 3, \dots, n)$ . Hence, this is invariant under the  $n!$  permutations of the  $n$  identical particles of the system. These symmetry operations will be considered in § 6.7, whereas in the next and following sections we shall discuss the properties of the point groups.

## 6.1 Cyclic Groups

The simplest possible point groups are the cyclic groups. They are generated by the rotations around an axis. A rotation axis is said to be of order  $n$  when a rotation around it by  $2\pi/n$  is a covering operation of the system of points given. Call  $C_{n,m}$  a rotation by  $2\pi m/n$  and  $C_n \equiv C_{n,1}$  a rotation by  $2\pi/n$ . Then  $C_{n,m} = C_n^m$  because  $C_{n,m}$  is equivalent to applying the rotation  $C_n$   $m$  times. Also  $C_n^n = E$  (rotation by  $2\pi$ ). Hence, the  $n$  rotations around an  $n$ -fold axis form a cyclic group of order  $n$ . Such a group is denoted with the symbol  $C_n$ .

The powers of a rotary reflection  $S_n$  (rotation by  $2\pi/n$  followed by the reflection  $\sigma_h$  on a plane perpendicular to the rotation axis) can also generate a cyclic group. When  $n$  is even this is a group of order  $n$  and it is called  $S_n$ . When  $n$  is odd the order of the group is  $2n$ , and the resulting group can be expressed as a direct product  $C_n \times C_2$ . This is so because  $S_n^n = (\sigma_h C_n)^n$



$= \sigma_h^n C_n^n = \sigma_h^n$ , and this latter is equal to  $E$  when  $n$  is even (so that  $n$  is the order of the group) and equal to  $\sigma_h$  when  $n$  is odd (so that  $S_n^{2n} = \sigma_h^2 = E$ , and  $2n$  is the order of the group)

Some further relations can be found for the groups  $S_n$  ( $n$  even). First, it is clear that  $S_2 \equiv i$ , so that  $S_2 = C_1$ . Also,  $S_n^{n/2}$  is equal to  $C_2$  if  $n/2$  is even, or to  $S_2 \equiv i$  if  $n/2$  is odd. In this latter case it can be readily seen that all the operations of  $S_{2n}$  ( $n$  odd) are either operations of  $C_n$  or products of them by  $i$ , that is  $S_{2n} = C_n \times C_2$  ( $n$  odd). These results are used in Table XI.

We shall now consider the actual geometry of a cyclic group. To have an  $n$ -fold axis we must have  $n$  identical figures symmetrically disposed in a plane perpendicular to the given axis. If these figures were just points (or spheres) we would have higher symmetry than the purely cyclic one; the plane that contains the  $n$  points, for instance would be a symmetry plane. To destroy all symmetry, except the cyclic one, we must start from the original set of  $n$  points and add to them suitable ornaments, that is other points that restrict the symmetry of each of the  $n$  figures and therefore that of the whole system. This is clear in Fig. 12, where we illustrate the groups  $C_2$  and  $S_2$ .

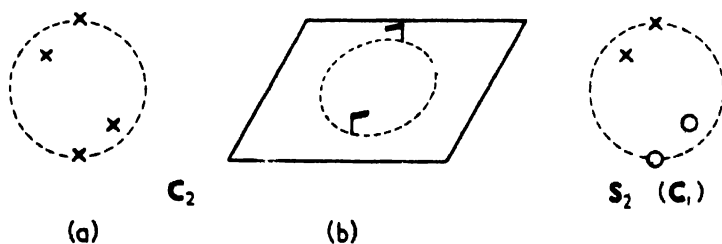


FIG. 12 Groups  $C_2$  and  $S_2(C_1)$ .  $\times$ , point above the plane of the drawing,  $\circ$ , point below the plane of the drawing. (a) and (b) represent both the group  $C_2$ , (b) being a perspective of the projection (a)

As the cyclic groups are abelian (§ 2.2) each element forms a class by itself, so that the order of the group,  $n$ , say, is equal to the number of its classes. Hence, the number of irreducible representation is also  $n$ . Since the sum of the squares of the dimensions of the  $n$  irreducible representations must be equal to  $n$ , all the representations must be one-dimensional. The irreducible representations themselves can be most easily obtained by the following argument.

Consider a cyclic group  $R, R^2, R^3, \dots, R^n \equiv E$ . We can use the notation  $R^m \equiv R_m$ , so that  $R_u R_v = R^u R^v = R^{u+v} = R_{u+v}$ . Therefore, the matrix representatives must satisfy the condition

$$D^k(R_u) D^k(R_v) = D^k(R_{u+v}),$$

which is the case when

$$D^k(R_m) = e^{ij_k \cdot (2\pi/n)m} \quad (128)$$

Here  $j_k$  is a variable that depends on the irreducible representation considered and carries the suffix  $k$  (which denotes the representation) as a reminder of this fact. The factor  $2\pi/n$  in the exponent is not essential and in fact various other factors or none at all are often used. We include it because if  $R_m$  is a rotation  $C_{n,m}$ , as defined before,  $(2\pi/n)m$  is the rotation angle (for which we shall use the symbol  $r_m$ ) and  $j_k$  turns out to have a particularly simple form with this factor. In fact,  $j_k$  can be further specified from the condition  $D^k(R_n) = D^k(E) = 1$ . As  $D^k(R_n) = \exp(ij_k 2\pi)$ ,  $j_k$  must be an integer:  $j_k = 1, 2, \dots$ . We shall also see that  $j_k + n$  gives the same representation as  $j_k$ :

$$e^{i(j_k+n) \frac{2\pi}{n} m} = e^{ij_k(2\pi/n)m} e^{i2\pi m} = D^k(R_m).$$

Therefore  $j_k$  can take only the  $n$  values  $1, 2, \dots, n$ . This is in agreement with our previous result, as these  $n$  values will correspond to the  $n$  possible irreducible representations. These are denoted with the index  $k$  that goes from 1 to  $n$ , so that we can just take  $j_k = k$ . Summarizing,

$$D^k(R_m) = e^{ikr_m}, \quad k, m = 1, 2, \dots, n; \quad r_m \equiv \frac{2\pi}{n} m \quad (129)$$

Examples of the use of this expression can be found in Table XVII.

The representations of direct products of cyclic groups are very easily obtained from (129). A direct product representation will be denoted by the multiple index  $k_1 k_2 \dots$ . Then

$$D^{k_1 k_2 \dots} (R_{m_1} R_{m_2} \dots) = \exp i(k_1 r_{m_1} + k_2 r_{m_2} + \dots).$$

It is convenient to define two vectors as follows:  $\mathbf{k} = k_1 \boldsymbol{\kappa}_1 + k_2 \boldsymbol{\kappa}_2 + \dots$ ,  $\mathbf{r}_m = r_{m_1} \boldsymbol{\tau}_1 + r_{m_2} \boldsymbol{\tau}_2 + \dots$ , where  $\boldsymbol{\kappa}_i$  and  $\boldsymbol{\tau}_j$  are unit vectors chosen so that:  $\boldsymbol{\kappa}_i \cdot \boldsymbol{\tau}_j = \delta_{ij}$ . Then the vector  $\mathbf{k}$  itself can be chosen to define the direct product representation and this is given as

$$D^{\mathbf{k}}(R_m) = e^{i\mathbf{k} \cdot \mathbf{r}_m}. \quad (130)$$

$\mathbf{r}_m$  can usually be given a direct meaning in the configuration space (this is the case for instance for the translation group of a crystal, when  $\mathbf{r}_m$  corresponds just to a three-dimensional translation) whereas  $\mathbf{k}$  is a vector defined in the so-called *reciprocal space*.

## 6.2 The Dihedral and Related Groups

The dihedral groups result when extra symmetry operations are added to those of the cyclic groups. They possess a *principal rotation axis*, i.e.,

one of higher order than any of the others of the group, and binary axes perpendicular to it. Related to the dihedral groups there are others that possess reflection planes through the principal axis. Before we show how these groups arise, we shall give their nomenclature, in Table XI, in a notation due to Schönflies.

TABLE XI  
CYCLIC, DIHEDRAL AND RELATED GROUPS<sup>a</sup>

Group	Characteristic symmetry elements	Crystallographic point groups
$C_n$	$n$ -fold axis only	$C_1, C_2, C_3, C_4, C_6$
$S_n$	$n$ -fold alternating axis only	$S_2(C_2), S_4, S_6(C_3)$
$C_{nh}$	$n$ -fold axis, reflection plane $\perp$ to it ( $\sigma_h$ )	$C_{1h}, C_{2h}, C_{3h}, C_{4h}, C_{6h}$
$C_{nv}$	$n$ -fold axis, $n$ reflection planes through it ( $\sigma_v$ )	$C_{2v}, C_{3v}, C_{4v}, C_{6v}$
$D_n$	$n$ -fold axis, $n$ binary axes $\perp$ to it (called $C'_2, C''_2, \dots$ )	$D_2, D_3, D_4, D_6$
$D_{nd}$	As for $D_n$ , reflection planes bisecting angles between binary axes ( $\sigma_d$ )	$D_{2d}, D_{3d}$
$D_{nh}$	As for $D_n$ , reflection plane $\perp$ to principal axis ( $\sigma_h$ )	$D_{2h}, D_{3h}, D_{4h}, D_{6h}$

<sup>a</sup> When the principal axis is placed vertically the  $\sigma_h$  plane is horizontal and the  $\sigma_v$  planes are vertical, which explains the use of the suffixes  $h$  and  $v$ . The suffix  $d$  stands for "diagonal."

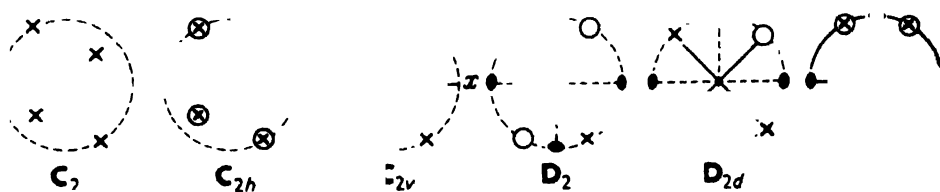


FIG. 13. Groups related to  $C_2$ . KEY  $\times$ , point above the plane of the drawing;  $\circ$ , point below the plane of the drawing. Broken circle: the plane of the figure is not a symmetry plane. Full circle: the plane of the figure is a symmetry plane ( $\sigma_h$ ).  $\bullet$ ,  $\bullet$ , binary axis. —, reflection plane perpendicular to the plane of the drawing. These conventions are standard for diagrams of this type, called *stereographic projections* (see Eyring, Walter and Kimball<sup>18</sup> for diagrams for all groups).

We can now see how these groups can be derived, which we do in Fig. 13 where, as an example we give all the groups related to  $C_2$  and the dihedral group  $D_2$ .

The symmetry of  $C_2$  can first be increased in two ways: we can add a symmetry plane  $\sigma_h(C_{2h})$  or we can add a vertical symmetry plane ( $\sigma_{vy}$  say). In this latter case (group  $C_{2v}$ ) another symmetry plane ( $\sigma_{vx}$ ) appears perpendicular to the first one, as it is clear from the figure. This also results from the following argument.  $C_{2x}$  multiplied by  $\sigma_{vy}$  must also be a symmetry operation of the group. As  $\sigma_{vy} = iC_{2x}$ , and  $i$  commutes with all the symmetry operations,  $C_{2x}\sigma_{vy} = iC_{2x}C_{2x} = iC_{2y} = \sigma_{vx}$ .

Analogously, on adding a binary axis perpendicular to  $C_{2x}$  we also introduce another, orthogonal both to it and to  $C_{2x}$ . This is the case in the group  $D_2$ . In its turn, the symmetry of  $D_2$  can be increased in two ways: we can add two diagonal  $\sigma_d$  planes, as in  $D_{2d}$ , or we can add reflection symmetry with respect to the plane of the figure, as in  $D_{2h}$ .

Notice that in  $D_{2d}$  the principal axis ( $z$ ) is also a fourfold alternating axis. If a similar drawing is done for  $D_{3d}$  it will be seen that the principal axis is now a sixfold alternating one. This is why  $D_{nd}$  groups do not appear as crystallographic point groups when  $n > 3$ , (cf. Table XI) because axes of order higher than six are not permitted for them.

It is useful to notice that the groups  $C_{2v}$  and  $C_{2h}$  can be derived from the dihedral group  $D_2$  through an isomorphism. In fact,  $D_2 = E + C_{2x} + C_{2x} + C_{2y}$  and  $C_{2x}C_{2y} = C_{2x}$ . If we substitute  $iC_{2x} = \sigma_y$  and  $iC_{2y} = \sigma_x$  for  $C_{2x}$  and  $C_{2y}$  in  $D_2$ , we obtain an isomorphic group, because  $iC_{2x}iC_{2y} = C_{2x}C_{2y} = C_{2x}$ . This group is  $C_{2v}$ . On the other hand, if we correlate  $C_{2x} \leftrightarrow i$ ,  $C_{2y} \leftrightarrow \sigma_h \equiv iC_{2x}$ , we have  $i\sigma_h = iiC_{2x} = C_{2x}$ , so that we also maintain the isomorphism. The group thus generated is  $C_{2h}$ .  $D_{2h}$  can also be expressed in terms of  $D_2$  as a direct product:  $D_{2h} = D_2 \times C_i$ . The remaining group of those given in Fig. 13, namely  $D_{2d}$  is related in the same manner not to  $D_2$  but rather to  $D_4$ , with which it is isomorphic. This could be expected because of the presence of the fourfold alternating axis.

The above considerations can also be applied to the other dihedral and related groups. This is so because the isomorphism discussed above results from the following general argument. The rotations around the principal axis of a dihedral group form an invariant subgroup of it. In fact, they clearly form a group. This is an invariant one because the binary rotations perpendicular to the principal axis leave the latter invariant, so that the conjugates of the principal rotations under the secondary ones are still principal rotations. (A more detailed proof of this fact can also be given.) If  $n$  is the order of the principal axis this is also the order of the invariant subgroup. The order of the dihedral group is  $2n$ , as there are  $n$  binary rotations. Hence, the index of the invariant subgroup  $C_n$  of  $D_n$  is 2, which means that it has two distinct co-sets only. That is, the factor

group  $D_n/C_n = C_n + C_n C'_2$ , where  $C'_2$  is any one of the secondary binary rotations. This means that the elements of  $D_n$  either belong to  $C_n$  or have the form  $C_r C'_2$ , where  $C_r \in C_n$ . We shall now show that the product of any two elements of the co-set  $C_n C'_2$  always belongs to  $C_n$ . In fact, in the product  $C_r C'_2 C_s C'_2$  the last three factors are the conjugate of  $C_s$  under  $C'_2$  (because the reciprocal of a binary rotation is the same binary rotation). Therefore  $C'_2 C_s C'_2 = C_t \in C_n$ , so that  $C_r C'_2 C_s C'_2 = C_r C_t \in C_n$ , which proves the proposition just enunciated. For brevity, call  $C_r$  the elements of  $D_n$  that belong to  $C_n$  and  $H_r$  those that belong to the co-set  $C_n C'_2$  (the latter are just the  $n$  secondary binary rotations). To establish an isomorphism, we notice that

$$C_r C_s = C_t \in C_n, \quad (131)$$

$$H_u H_v = C_w \in C_n, \quad (132)$$

$$C_r H_s = C_r C_s C'_2 = C_t C'_2 = H_t. \quad (133)$$

Hence, we can obtain an isomorphism by establishing the correspondence

$$C_r \leftrightarrow C_r \text{ for all } C_r \in C_n,$$

$$H_u \leftrightarrow \iota H_u \text{ for all } H_u \in C_n C'_2$$

In fact, (131) is maintained. Also,

$$H_u H_v \leftrightarrow \iota H_u \iota H_v = H_u H_v = C_w \leftrightarrow C_w,$$

which shows that (132) is kept. Finally, from (133)

$$C_r H_s \leftrightarrow C_r \iota H_s = \iota C_r H_s = \iota H_t \leftrightarrow H_t.$$

It is clear that we can substitute  $\sigma_h$  (which commutes with all the operations of the dihedral groups) for  $\iota$  in the above. Brief consideration shows, however, that the group obtained is the same as before.

A second way to generate an isomorphism with a dihedral group is in a sense the converse of the above one. We start by establishing the correspondence:

$$C_r \leftrightarrow C_r \quad (r \text{ even}),$$

$$C_r \leftrightarrow \iota C_r \quad \text{or} \quad \sigma_h C_r \quad (r \text{ odd}).$$

The group thus generated is still an invariant subgroup, with an alternating axis. If we form the co-sets of it with  $C'_2$  as before, we can see at once that we obtain a group isomorphic with the original one. As an example, the invariant subgroup of  $D_6$  is  $E, C_6^+, C_3^+, C_2, C_3^-, C_6^-$ . We take the operation  $\sigma_h$  to generate the isomorphism, so that the corresponding subgroup is  $E, S_6^+, C_3^+, \iota C_3^-, S_6^-$  and the group generated by this and its co-set with  $C'_2$  is  $D_{3d}$ . When the operation  $\iota$  is used instead of  $\sigma_h$  the invariant subgroup is  $E, S_3^-, C_3^+, \sigma_h C_3^-, S_3^+$  (because,  $\iota C_6^\pm = S_3^\mp$ ). The group thus generated is  $D_{3h}$ , also isomorphic with  $D_6$ .

### 6.3 The Cubic Groups

The group of all the symmetry operations of a regular tetrahedron is called  $T_d$  in the Schönflies notation and that of a regular cube  $O_h$ . By adding ornaments to these figures, exactly as we did before, the full symmetry can be reduced, as shown in Fig. 14.

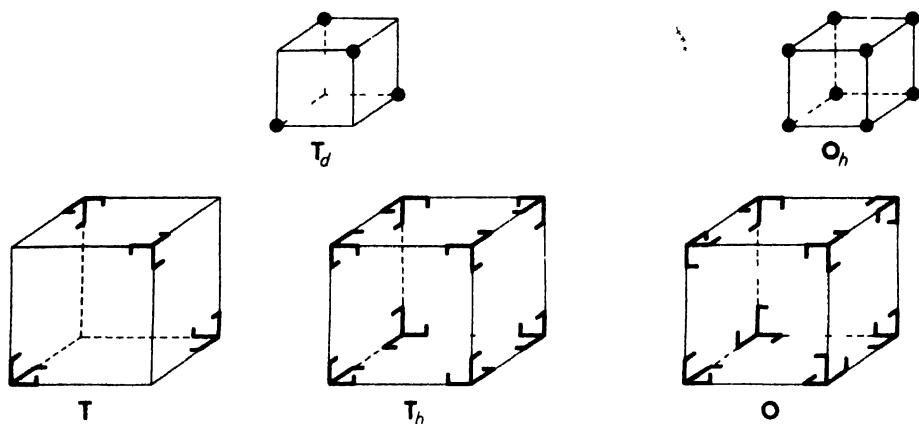


FIG. 14. The cubic groups.

$T$  contains just the subgroup of the pure rotations of the regular tetrahedron, i.e., the three binary axes (perpendicular to the faces of the cube drawn in the figure) and the four ternary axes along the diagonals of the cube. The diagonal symmetry planes of the tetrahedron disappear, as well as the fourfold rotary reflections around the axis perpendicular to the faces of the cube.  $T_h$  results from adding just the inversion operation to those of  $T$ , that is,  $T_h = T \times C_i$ . It should be noticed that it has not cubic symmetry yet, as the  $C_4$  axes are missing. Now, however, as in the full cube but in contrast to the tetrahedron, the planes parallel to the bases of the cube and midway between them are symmetry planes. This is as expected, as they are given by the products of the binary rotations of  $T$  by the inversion.  $O$  is the subgroup of the pure rotations of the full cubic group  $O_h$  and therefore contains the characteristic system of three fourfold axes. The symmetry planes disappear because there is no inversion symmetry. The full cubic group  $O_h$  is given by the direct product  $O_h = O \times C_i$ .

### 6.4 The Representations of the Point Groups

The characters of the irreducible representations of the point groups can be obtained by the method given in § 3.10, which we have already applied to  $C_{3v}$ . The character tables for the crystallographic point groups

are given in the tables at the end of this chapter (§ 7). The notation used in them to designate the irreducible representations is one due to Placzek and Mulliken (see Mulliken<sup>21</sup>) and it is summarized in Table XII.

The representations themselves can be obtained by the method given in § 1. A more general method has been discussed by Altmann<sup>23</sup> and they are listed in full by Seitz<sup>24</sup>

TABLE XII  
NOTATION FOR THE IRREDUCIBLE REPRESENTATIONS OF POINT GROUPS

Property represented	Symbol	Meaning
Degeneracy of representation	$A, B$	Non degenerate
	$E$	Double degenerate
	$T$	Triple degenerate
	$G$	Fourfold degenerate
	$H$	Fivefold degenerate
Symmetry with respect to the principal axis	$A$	Symmetrical
	$B$	Antisymmetrical
Symmetry with respect to inversion	Suffix $g$	Symmetrical (in German <i>gerade</i> )
	Suffix $u$	Antisymmetrical (in German <i>ungerade</i> )
	Used with any of the above symbols	
Symmetry with respect to $\sigma_h$	Prime '	Symmetrical
	Double prime ''	Antisymmetrical
	Used with any of the above symbols	
Symmetry with respect to the secondary binary axes	Suffix 1	The most symmetrical of the $A$ or $B$ representations
	Suffixes 2, 3	Other $A$ or $B$ representations
	Used with symbols $A$ or $B$	
Transformation properties of the spherical harmonics (see § 6 5)	Suffix 1	Representation to which there belongs the spherical harmonic with $m = 1$
	Suffix 2	Representation to which there belongs the spherical harmonic with $m = 2$
	Used with symbol $E$	

### 6.5 The Bases for the Representations of the Point Groups: Transformation Properties of the Spherical Harmonics

All the operations of the point groups can be expressed in terms of pure rotations multiplied at most by the inversion. It is enough for this purpose to use relations such as

$$\sigma = iC_2, \quad S_8^\pm = iC_8^\mp, \quad S_4^\pm = iC_4^\mp.$$

We shall therefore consider first the pure rotations and shall take into account at a later stage the effect of the inversion operation.

The spherical harmonics are the natural functions to use to form bases to represent rotations. This is so because the spherical harmonics form a complete set of functions of position on the surface of the unit sphere. This means that an arbitrary function of position on the unit sphere, subject to some simple continuity conditions, can always be represented as a series of terms in spherical harmonics. The transform  $RY_l^m(\theta, \phi)$  of a spherical harmonic  $Y_l^m(\theta, \phi)$  under a rotation  $R$  will clearly be a function of position on the unit sphere and as such given by a linear combination of spherical harmonics. Short consideration shows also that the rotated spherical harmonic must be one of the same order  $l$  as the original one. Therefore,

$$RY_l^m(\theta, \phi) = \sum_{-l}^{+l} Y_l^{m'}(\theta, \phi) D(R)_{m'}^m \quad (134)$$

and the coefficients  $D(R)_{m'}^m$  form as before a matrix representative  $D(R)$  of dimension  $2l + 1$ . The corresponding representation is not, in general, irreducible and we want now to find which are the irreducible representations into which it reduces. This problem is solved by means of the standard technique described in § 3.9: the characters of the reducible representation are obtained for all the classes of the group, and from these, and the tabulated characters of the irreducible representations, the number of times that each irreducible representation is contained in the reducible one can be deduced (formula 57 of § 3.9).

To obtain the characters for the reducible representation, let us first consider a rotation  $R(\alpha)$  by  $\alpha$  around the polar axis ( $z$ ) of the spherical harmonics. As, leaving aside a normalization factor,

$$Y_l^m(\theta, \phi) = P_l^m(\cos \theta) e^{im\phi},$$

we have

$$R(\alpha) Y_l^{m'}(\theta, \phi) = Y_l^{m'}(\theta, \phi + \alpha) = P_l^{m'}(\cos \theta) e^{im'(\phi + \alpha)} = e^{im'\alpha} Y_l^{m'}(\theta, \phi). \quad (135)$$



On using this result for all the values  $m' = -1, \dots, +1$ , we obtain

$$D[\mathbf{R}(\alpha)] = \begin{vmatrix} e^{-i\alpha} & & \\ & e^{-i(l-1)\alpha} & \\ & & e^{i\alpha} \end{vmatrix}$$

so that the character  $\chi'(\alpha)$  is

$$\begin{aligned} \chi'(\alpha) &= \sum_{m=-l}^{+l} e^{im\alpha} = \frac{\sin(l + \frac{1}{2})\alpha}{\sin \frac{1}{2}\alpha} & \alpha \neq 0, \\ &= 2l + 1, & \alpha = 0 \end{aligned} \quad (136)$$

(notice that the summation is just that of a geometric progression)

Now let us consider rotations around an axis that does not coincide with the polar one ( $z$ ). Such rotations will have to be considered always in forming a representation of a point group because, in order to write down the spherical harmonics, coordinate axes must first be chosen and they must be the same for all the operations of the group. For instance, if in a dihedral group the polar axis is chosen to coincide with the principal one, the secondary binary rotations are around axes that are perpendicular to  $z$ . To have the representation in full, a more elaborate formula than (135) will be required (see Wigner<sup>1</sup>). Formula (136) is still valid, however, to obtain the character. This is so because we know that the characters are invariant under a unitary transformation, so that the polar axis can always be rotated so as to coincide with that of the particular rotation considered.

The last step to make the treatment quite general is the introduction of the inversion symmetry, for which we must consider the transformation properties of the spherical harmonics under it. These are very simple because as the spherical harmonic of order  $l$  is a homogeneous polynomial in  $x$ ,  $y$  and  $z$  of order  $l$ , it must be invariant under inversion if  $l$  is even, and must be multiplied by  $-1$  if  $l$  is odd. That is,

$$iY_l^m(\theta, \phi) = (-1)^l Y_l^m(\theta, \phi)$$

Therefore, for the operations that contain the inversion, expression (136) for the character must be multiplied by  $(-1)^l$ .

We consider as an example the group  $C_{3v}$ . The values of  $\alpha$  are 0 for  $E$ ,  $2\pi/3$  for  $C_3$  and  $2\pi/2$  for  $\sigma_v = iC_2$ . The characters required are obtained very easily and are listed in Table XIII.

TABLE XIII  
CHARACTERS OF THE  $(2l + 1)$ -DIMENSIONAL REPRESENTATIONS OF  $C_{3v}$

$l$	$E$	$2C_3$	$3\sigma_v$
0	1	1	1
1	3	0	1
2	5	-1	1
3	7	1	1

On using the characters given in Table XIII, the character table for  $C_{3v}$  (Table XX) and formula (57) of § 3.9, we obtain the number of times that each irreducible representation is contained in the reducible one. These numbers are listed in Table XIV, which we call the *partition table* of the spherical harmonics.

TABLE XIV  
PARTITION TABLE OF THE SPHERICAL HARMONICS FOR  $C_{3v}$

$l$	$A_1$	$A_2$	$E$
0	1		
1	1		1
2	1		2
3	2	1	2

To extend this table from the line  $l = 3$  onwards, it is enough to use this rule: take the line  $l - 3$  and add to it as many units as the dimension of the corresponding irreducible representation. Its proof is very simple (see also Altmann<sup>23</sup>).

The results obtained in Table XIV, first given in a classical paper by Bethe,<sup>20</sup> are of physical importance for the following reason. Consider, say, a nitrogen atom which has the ground state configuration  $1s^2 2s^2 2p^3$ . The three  $2p$  states are degenerate in the free atom. Suppose now that the nitrogen atom is placed in a field of  $C_{3v}$  symmetry, as it happens when it is surrounded by the three hydrogen atoms of the ammonia molecule. Table XIV shows that now two of the  $p$  states ( $l = 1$ ) belong to the representation  $E$ , and the other one to  $A_1$ . As there corresponds one energy eigenvalue to each irreducible representation, we conclude that the triply degenerate level corresponding to the  $p$  orbitals of the free atom splits up in the  $C_{3v}$  field in

two levels, one single and one double degenerate. Similar considerations are crucial in the theory of metal complexes.

It is useful to notice that the result just obtained agrees with the observation made in § 1.7 that the representation spanned by the spherical harmonics in real form  $p_x, p_y$  and  $p_z$  splits up into two, one spanned by  $p_z$  and the other, double degenerate, by  $p_x$  and  $p_y$ . In fact, the results of the partition table combined with the use of the technique employed in § 1.7 permits us to determine not only how the spherical harmonics separate among the representations but also which are the spherical harmonics that correspond to each representation. These symmetry assignments of the spherical harmonics are very useful in a variety of fields — molecular structure (hybrids, crystal field theory, etc.), molecular vibrations, solid state (expansion of the wave function in the cellular method), etc.

We shall discuss in full another example of a symmetry assignment of a spherical harmonic, now of order 2. We see from Table XIV that the five harmonics of order 2 are distributed as follows: one in  $A_1$ , and two double degenerate pairs in  $E$ . We first take one of these five harmonics, for simplicity given in real form as  $d_{x^2-y^2}$  (see, e.g., Table XVI). This transforms just as  $x^2 - y^2$ . The transformation properties of  $x$  and  $y$  are exactly those of  $p_x$  and  $p_y$  discussed in § 1.7 and given in matrix form in Table IV. We list explicitly the transforms of  $x$  and  $y$  in the second and third column of Table XV. From these, the transforms of  $x^2 - y^2$  can be readily worked out and are given in the fourth column of the table. As we see that the transforms of  $x^2 - y^2$  are given in terms of itself and the spherical harmonic  $xy$ , we expect this latter to be the partner of  $x^2 - y^2$  in a double degenerate representation;  $x^2 - y^2, xy$  would then be one of the two degenerate pairs belonging to  $E$ . To confirm this we find the transforms of  $xy$  in the fifth column of the table. We could now write down explicitly the matrix representation constructed on the basis  $\langle x^2 - y^2, xy |$ . It is enough for our purposes, however, to determine the corresponding characters. It is easy to see, by imagining the matrices written in full, that the characters are the sums of the coefficient of  $(x^2 - y^2)$  in the  $x^2 - y^2$  column plus the coefficient of  $xy$  in the  $xy$  column. They are listed in the last column of the table and they coincide with those of the representation  $E$  (Table XX). Therefore the basis  $\langle x^2 - y^2, xy |$  spans the representation  $E$ .

We can proceed in the same manner to find the remaining symmetry assignments of the spherical harmonics given in Table XX for the group  $C_{3v}$ . This method, however, becomes prohibitively difficult for the higher order spherical harmonics. The symmetry assignments given in the tables at the end of this chapter have therefore been obtained by a more general

method (Altmann<sup>23</sup>). In obtaining and using these symmetry assignments it must be remembered that they depend crucially on the position of the axes chosen with respect to the symmetry elements of the group.

TABLE XV  
SYMMETRY ASSIGNMENT OF  $x^2 - y^2$ ,  $xy$  FOR  $C_{3v}$

R	$x$	$y$	$x^2 - y^2$	$xy$	$\chi(R)$
E	$x$	$y$	$x^2 - y^2$	$xy$	2
$\sigma_1$	$x$	$-y$	$x^2 - y^2$	$-xy$	0
$\sigma_2$	$-\frac{1}{2}x - \frac{\sqrt{3}}{2}y$	$\frac{\sqrt{3}}{2}x + \frac{1}{2}y$	$-\frac{1}{2}(x^2 - y^2) + \sqrt{3}xy$	$\frac{\sqrt{3}}{4}(x^2 - y^2) + \frac{1}{2}xy$	0
$\sigma_3$	$-\frac{1}{2}x + \frac{\sqrt{3}}{2}y$	$\frac{\sqrt{3}}{2}x - \frac{1}{2}y$	$-\frac{1}{2}(x^2 - y^2) - \sqrt{3}xy$	$-\frac{\sqrt{3}}{4}(x^2 - y^2) + \frac{1}{2}xy$	0
$C_3^+$	$-\frac{1}{2}x - \frac{\sqrt{3}}{2}y$	$\frac{\sqrt{3}}{2}x - \frac{1}{2}y$	$-\frac{1}{2}(x^2 - y^2) + \sqrt{3}xy$	$-\frac{\sqrt{3}}{4}(x^2 - y^2) - \frac{1}{2}xy$	-1
$C_3^-$	$-\frac{1}{2}x + \frac{\sqrt{3}}{2}y$	$\frac{\sqrt{3}}{2}x + \frac{1}{2}y$	$-\frac{1}{2}(x^2 - y^2) - \sqrt{3}xy$	$\frac{\sqrt{3}}{4}(x^2 - y^2) - \frac{1}{2}xy$	-1

## 6.6 Transformation Properties of Rotations

It is often useful, as for instance in the study of vibrational spectra, to possess the transformation properties of rotations around the coordinate axes  $x, y, z$  under the operations of a group. This is simple, if we use the representation of a rotation by a vector. A rotation is represented by a vector in the direction of the positive half of the  $z$ -axis (rotation axis) when the rotation is positive (see § 1.3) and in the opposite direction when the rotation is negative (Fig. 15). It is important to be aware

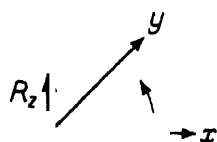


FIG. 15. Representation of a rotation by a vector.

of the fact that such a vector is not a genuine one but rather a pseudovector, the transformation properties of which are not identical with those of ordinary vectors. In fact whereas a vector such as  $\mathbf{R}_x$  in the figure would appear to be invariant under a reflection in the plane  $yz$ , the rotation vector  $\mathbf{R}_x$  is inverted (which coincides with the fact that the rotation considered goes from a positive one — i.e., a rotation that takes the positive half of the  $x$ -axis into the positive half of the  $y$ -axis — into a negative one when  $x \rightarrow -x$ ).

All this is quite clear when the proper definition of the rotation vector as a vector product is used. Then  $\mathbf{R}_x = \mathbf{x} \times \mathbf{y}$  and similarly for the other

vectors. When we reflect on the  $yz$  plane,  $x \rightarrow -x$  and  $y \rightarrow y$  so that we see at once that  $\mathbf{R}_x \rightarrow -\mathbf{R}_x$ .

The crucial difference between vector products and ordinary vectors is that, whereas ordinary vectors change sign when the inversion operation is effected on the coordinate axes, these pseudo vectors are invariant. This is clear from the above definition for  $\mathbf{R}_x$  as a vector product. We obtain therefore the following simple rule. The rotations  $\mathbf{R}_x, \mathbf{R}_y$ , and  $\mathbf{R}_z$  transform exactly like  $x, y$ , and  $z$  respectively under all pure rotations. The transformation matrices of  $x, y$ , and  $z$  must be multiplied by  $-1$  to give the transformation of  $\mathbf{R}_x, \mathbf{R}_y$ , and  $\mathbf{R}_z$  respectively, under the operations that can be expressed as a pure rotation times the inversion. As we know how to find the transformation properties of  $x, y$ , and  $z$  we can obtain at once those for the rotations, (cf. Tables XVII—XXIV).

### 6.7 The Symmetric Group

The  $n!$  permutations of  $n$  objects clearly form a group. This is called the *symmetric group*. As an example, consider the permutations of three objects 1,2,3. A permutation that replaces 1 by 3, 3 by 1, and leaves 2 invariant will be denoted with the symbol

$$P_1 = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix}$$

The product of two such permutations is obviously another permutation. For instance, consider

$$P_2 = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix}$$

Then,

$$P_2 P_1 = \begin{pmatrix} 2 & & 2 \\ 2 & & 1 \end{pmatrix} = P_3.$$

(Notice that the permutations must be applied from the right to the left. The opposite convention is used by some authors.)

We have met these permutations before, as one way of expressing the operations of  $C_{3v}$ . From Table I of § 1.7 we can see that  $P_1 \leftrightarrow \sigma_2$ ,  $P_2 \leftrightarrow C_3^+$  and  $P_3 \leftrightarrow \sigma_3$ . Hence, the last equation just corresponds to the equality  $C_3^+ \sigma_2 = \sigma_3$  (cf. Eq. 24 of § 1.7).

Every permutation can be expressed as a product of permutations that involve separate elements and which are called *cycles*. For instance,

$$P_1 = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 3 \\ 3 & 1 \end{pmatrix} \begin{pmatrix} 2 \end{pmatrix}$$

These cycles must be selected so that they cannot be further decomposed in this manner. Some permutations are such that they contain only one cycle and, accordingly, are called *cyclic permutations*. Such is the case with  $P_2$  (notice that this, in fact, corresponds to the rotation  $C_3^+$  in  $C_{3v}$ ).

A convenient notation for a cycle is

$$(abc\dots z) \equiv \begin{array}{l} abc\dots z \\ bcd\dots a \end{array}$$

We can write:  $P_1 = (1\ 3)(2)$ ,  $P_2 = (1\ 3\ 2)$ .

We shall now consider the classes of the symmetric group. In our previous nomenclature, the first row of the original symbol for a permutation can be considered as the basis on which the permutation is applied. Consider now the permutation

$$P_4 = \begin{array}{c} 2 \\ 3 \end{array} = (2\ 3)(1)$$

The symmetric group will always include a permutation such that  $1 \rightarrow 2$ ,  $2 \rightarrow 1$ ,  $3 \rightarrow 3$ . When this is effected on the basis 1,2,3,  $P_4$  goes into

$$\begin{pmatrix} 2 & 1 & 3 \\ 2 & 3 & 1 \end{pmatrix} = (2)(1\ 3) = P_1.$$

As  $P_4$  goes over into  $P_1$  by transforming the basis under an operation of the group,  $P_4$  and  $P_1$  must belong to the same class. (In fact,  $P_1$  and  $P_4$  correspond respectively to the operations  $\sigma_2$  and  $\sigma_1$  of  $C_{3v}$ , which belong to the same class.) It is easy to convince oneself that a transformation of this type is possible if and only if the two permutations have cycles of the same length. Hence, permutations that have cycles of the same length belong to the same class.

The length of the cycles of a permutation of  $n$  elements is given by a partition of the number  $n$  in a sum of integers. Hence, the number of classes of the group of permutations of order  $n!$  will be the number of such partitions of the number  $n$ . For instance, in the example considered,  $n = 3$  and

$$\begin{aligned} 3 &= 1 + 1 + 1 \\ &= 2 + 1 \\ &= 3 \end{aligned}$$

so that we shall have three classes. This agrees with our previous result for  $C_{3v}$ .

Every permutation can be written as a product of cycles of length 2, which are called *transpositions*.

$$P_2 = \begin{array}{ccc} 1 & 2 & 3 \\ 3 & 1 & 2 \end{array} \equiv (31)(32).$$

A permutation is called *even* or *odd* when the number of transpositions in which it is expressed is even or odd respectively.

The product of two even permutations is clearly an even permutation. Hence, the even permutations form a subgroup of order  $n!/2$  of the symmetric group of order  $n!$ , which is called the *alternating group*. This is an invariant subgroup of the symmetric group, because under either left or right multiplication by any odd permutation it must give the set of  $n!/2$  odd permutations, so that the right and left co-sets of the alternating group are equal.

The even permutations of the symmetric group of order  $3!$  are the identity (1) (2) (3),  $P_2 = (132)$ , and  $P_3 = (123)$ . That they form an invariant subgroup agrees with the fact that they correspond to the operations  $E$ ,  $C_3^+$  and  $C_3^-$  respectively which form an invariant subgroup of  $C_{3v}$ .

The fact that the symmetric group possesses an invariant subgroup of index 2 has an immediate consequence on the form of its irreducible representations. In fact, represent by  $A_i$  and  $B_j$  an even and odd permutation respectively ( $i, j = 1, 2, \dots, n!/2$ ). We have  $A_i B_j = B_k$ , and  $B_i B_j = A_l$ . Suppose now that we have a representation such that  $D(A_i)D(B_j) = D(B_k)$ , and  $D(B_i)D(B_j) = D(A_l)$ . We can see at once that, if we multiply the matrices  $D(B)$  by  $-1$  the multiplication rules are still preserved. We obtain in this manner a new representation called the *associate representation* of the original one.

## 7. Tables of Characters for the Point Groups

We give in this section tables of characters for all the crystallographic point groups. They include the symmetry assignments of the spherical harmonics, which are given, for all except the cubic groups, by the values of  $l$  and  $m$  (all  $l$  and  $m$ ) that are permitted in each representation. To facilitate the identification, the lower order spherical harmonics, corresponding to  $l = 1, 2$ , and  $3$  ( $p$ ,  $d$  and  $f$  functions respectively) are explicitly given in the tables, in cartesian coordinates. The  $p$  functions, that is,  $p_x$ ,  $p_y$ , and

$p_x$  are therefore given as  $x$ ,  $y$ , and  $z$  respectively, and their transformation properties coincide with those for the corresponding coordinates  $x$ ,  $y$ , and  $z$ . The rotations  $R_x$ ,  $R_y$  and  $R_z$  are assigned as shown in § 6.6. No general rule can be given for the values of  $l$  and  $m$  that are permitted in the cubic groups and the  $p$ ,  $d$ , and  $f$  functions only are listed. Full tables up to  $l = 6$  are given by Altmann.<sup>23</sup> Symmetry assignments for the icosahedral group are given by Cohan.<sup>25</sup> Prior to the tables we give a summary of the formulas for the spherical harmonics and some notes.

### 7.1 Formulas for the Spherical Harmonics

The normalized spherical harmonics are

$$Y_l^m(\theta, \phi) = \sqrt{\left(\frac{2l+1}{4\pi}\right) \frac{(l-|m|)!}{(l+|m|)!}} P_l^m(\cos \theta) e^{im\phi} \quad (137)$$

Unnormalized spherical harmonics  $\mathcal{Y}_l^m(\theta, \phi)$  are often used

$$\mathcal{Y}_l^m(\theta, \phi) = P_l^m(\cos \theta) e^{im\phi} \quad (138)$$

The spherical harmonics can be expressed in real form as follows:

$$Y_l^{m,c}(\theta, \phi) = (Y_l^m + Y_l^{-m})/\sqrt{2} = \sqrt{\left(\frac{2l+1}{2\pi}\right) \frac{(l-|m|)!}{(l+|m|)!}} P_l^m(\cos \theta) \cos m\phi \quad (139)$$

$$Y_l^{m,s}(\theta, \phi) = -i(Y_l^m - Y_l^{-m})/\sqrt{2} = \sqrt{\left(\frac{2l+1}{2\pi}\right) \frac{(l-|m|)!}{(l+|m|)!}} P_l^m(\cos \theta) \sin m\phi \quad (140)$$

$$\mathcal{Y}_l^{m,c}(\theta, \phi) = \frac{1}{2}(\mathcal{Y}_l^m + \mathcal{Y}_l^{-m}) = P_l^m(\cos \theta) \cos m\phi \quad (141)$$

$$\mathcal{Y}_l^{m,s}(\theta, \phi) = -\frac{i}{2}(\mathcal{Y}_l^m - \mathcal{Y}_l^{-m}) = P_l^m(\cos \theta) \sin m\phi \quad (142)$$

The lower order spherical harmonics ( $l = 1, 2, 3$ ) are expressed in cartesian coordinates in Table XVI.

The symbols given in the first column correspond to the unnormalized spherical harmonics defined in (141) and (142). If the expressions given in the second column are multiplied by the factor  $N$  derived from the last one, the normalized spherical harmonics defined in (139) and (140) are obtained. The symbol given in the third column is used in the tables to denote normalized or unnormalized functions indifferently, except for the cubic groups where they can be identified with the unnormalized functions only.



TABLE XVI  
THE  $p$ ,  $d$ , AND  $f$  FUNCTIONS

Spherical harmonic	Expression in Cartesian coordinates	Symbol used in the tables	$N^a$
$\mathcal{Y}_1^{1,c}$	$x$	$x$	$3/4\pi$
$\mathcal{Y}_1^{1,s}$	$y$	$y$	$3/4\pi$
$\mathcal{Y}_1^0$	$z$	$z$	$3/2\pi$
$\mathcal{Y}_2^0$	$\frac{1}{2}(3z^2 - 1)$	$z^2$	$5/2\pi$
$\mathcal{Y}_2^{1,c}$	$3zx$	$zx$	$5/12\pi$
$\mathcal{Y}_2^{1,s}$	$3yz$	$yz$	$5/12\pi$
$\mathcal{Y}_2^{2,c}$	$3(x^2 - y^2)$	$x^2 - y^2$	$5/48\pi$
$\mathcal{Y}_2^{2,s}$	$6xy$	$xy$	$5/48\pi$
$\mathcal{Y}_3^0$	$\frac{1}{2}(5z^3 - 3z)$	$A$	$7/2\pi$
$\mathcal{Y}_3^{1,c}$	$\frac{3}{2}(5z^2x - x)$	$B$	$7/24\pi$
$\mathcal{Y}_3^{1,s}$	$\frac{3}{2}(5z^2y - y)$	$C$	$7/24\pi$
$\mathcal{Y}_3^{2,c}$	$15(x^2z - y^2z)$	$D$	$7/240\pi$
$\mathcal{Y}_3^{2,s}$	$30xyz$	$L$	$7/240\pi$
$\mathcal{Y}_3^{3,c}$	$15(x^3 - 3y^2x)$	$F$	$7/1440\pi$
$\mathcal{Y}_3^{3,s}$	$15(3x^2y - y^3)$	$G$	$7/1440\pi$

## 7.2 Notes to the Tables

*Disposition of the tables.* The first row of the tables gives the name of the point group, in the notation of Table XI, § 6.2, followed by the operations of it denoted by the symbols explained in § 1.3 and Table XI. Only one element of each class is listed and the number of elements in the class is denoted by a numeral that precedes the symbol of the element.

The first, second, and third columns of the tables give the symmetry assignments for the  $f$ ,  $d$ , and  $p$  functions, which are denoted with the symbols given in Table XVI, respectively. The  $s$  functions are not listed as they always belong to the totally symmetrical representation. When two or three harmonics are given inside a bracket, they form a basis for a doubly or a triply degenerate representation. The third column gives also the symmetry properties of the rotations  $R_x$ ,  $R_y$ ,  $R_z$  around the  $x$ ,  $y$ ,  $z$  axes (see § 6.6).

The symbols in the fourth column name the irreducible representations in the notation of Table XII, § 6.4. (The letters  $A$ ,  $B$ ,  $E$  used in the first column of the tables should not be confused with the same letters that appear in the fourth column as names of the irreducible representations).

The columns of the tables that follow after the last class of the group give the symmetry assignments of the spherical harmonics of all orders, as explained below.

*Axes.* A right-handed system of axes is always used.

When the identification of the spherical harmonics would otherwise be ambiguous, the axes are oriented with respect to the symmetry elements of the group, as indicated in a footnote to the corresponding table.

When nothing is stated about the axes, it is enough to take  $z$  in the direction of the principal rotation axis.

*Notation for  $l$  and  $m$ .* If  $a$  is the number in brackets printed in the tables underneath  $m$ , the latter is given mod  $a$ , i.e., the values  $m \pm a$ ,  $m \pm 2a$ ,  $m \pm 3a, \dots$ , can be used. The symbol  $(+a)$  means that the plus sign only can be used in the above succession (we say that  $m$  is given mod  $(+a)$ ).

$l$  is given mod  $(+2)$  throughout the tables.

When no value of  $l$  is given in a table or part of it, it means that there is no restriction on the value of  $l$  to be used in the spherical harmonics.

*Form of the Spherical Harmonics.* The values  $l$  and  $m$  of the spherical harmonics in imaginary form (Eq. 137 and 138) are given in the corresponding columns. In the one-dimensional representations of the dihedral and related groups the spherical harmonics appear as combinations  $Y_l^m + Y_l^{-m}$  or  $Y_l^m - Y_l^{-m}$ , so that they can be expressed in real form (Eqs. 139–142) and the corresponding superscripts (that is, the  $\phi$  dependence of the harmonics) are given in the column headed  $\phi$ . In the degenerate representations of the dihedral and related groups, the spherical harmonics appear in complex form, but  $Y_l^m$  and  $Y_l^{-m}$  always come together (for example, in the representation  $E$  of  $D_3$  we have  $Y_1^1$  and  $Y_1^{-1}$ , this latter corresponding to  $m = 2 - 3 = -1$ ) so that they can be converted into a degenerate pair of harmonics in real form. The  $\phi$ -dependence is now represented with the symbol  $(c, s)$ . For the spherical harmonics  $Y_l^{m,c}$  and  $Y_l^{m,s}$ ,  $m$  can take positive values only, hence the use of the mod  $(+a)$  convention for it.

The harmonics  $Y_l^m$  and  $Y_l^{-m}$  always appear together in the same real representations of the cyclic and related groups (cf. the example for  $C_{3h}$  below). It is therefore possible to transform them into their real and imaginary parts, which we do to write down the  $p$ ,  $d$ , and  $f$  functions that belong to these representations. In the complex representations of these groups (as well as of  $T$ ),  $Y_l^m$  and  $Y_l^{-m}$  never come together but rather one in each of the representations that form a conjugate pair. Hence, it is not possible to write the bases of these representations in real form. It is customary, however, to pair such representations so as to combine  $Y_l^m$  and  $Y_l^{-m}$  in the appropriate manner. We have done so in writing the  $p$ ,  $d$ , and  $f$  functions.

For example, the set  $(x^2 - y^2, xy)$  in  $C_{3h}$ , written by the side of the first of the representations of the pair named  $E'$ , has been obtained by pairing  $Y_2^2$  from this representation with  $Y_2^{-2}$  from the following one. It must be remembered therefore that such pairs correspond always to two representations, which are easily identified from the table, and that the true bases for the complex representations are the spherical harmonics in complex form.

The spherical harmonics for the cubic groups are given as linear combinations of the  $Y_l^m$  and it is not possible to list the permitted values of  $l$  and  $m$ , for all  $l$  and  $m$ , as we do for the other groups. An exception to this is the representation  $T$  of  $T$ , for which such a list is possible.

*Normalization of the Spherical Harmonics.* Except for the cubic groups, the spherical harmonics can be taken from the tables in normalized or unnormalized form. Correspondingly, the  $p$ ,  $d$ , and  $f$  functions can be used with or without the normalization factors listed in Table XVI. For the cubic groups the  $p$ ,  $d$ , and  $f$  functions are given in unnormalized form. If necessary, they can be easily normalized.

*Direct Product Groups.* If a group  $G'$  is given as a direct product of the form  $G \times C_n$ , an irreducible representation  $M$  of  $G$  goes into  $M_g$  and  $M_u$  of  $G'$ . The spherical harmonics belonging to these representations are those of even and odd order, respectively, that belong to the representation  $M$  of  $G$ .

*Examples of the Use of the Tables.* Take the representation  $A'$  of  $C_{3h}$ . From the table, the spherical harmonics belonging to it are

$$Y_0^0, Y_2^0, Y_4^0, Y_6^0, Y_8^0, \dots; Y_6^6, Y_8^6, Y_{10}^6, \dots; Y_3^3, Y_5^3, \dots$$

The spherical harmonics belonging to the representation  $A_1''$  of  $D_{3h}$  are

$$P_4^3(\cos \theta) \sin 3\phi, P_6^3(\cos \theta) \sin 3\phi, P_8^3(\cos \theta) \sin 3\phi, \\ P_{10}^3(\cos \theta) \sin 3\phi, \dots, P_{10}^9(\cos \theta) \sin 9\phi, \dots, P_7^6(\cos \theta) \sin 6\phi, \dots$$

TABLE XVII  
THE GROUPS  $C_n$  ( $n = 2, 3, 4, 6$ )

$C_2$			$E$	$C_2$	$m$ (2)
$A, D, E$	$z^2, x^2 - y^2, xy$	$z; R_z$	$A$	1    1	0
$B, C, F, G$	$yz, yz$	$x, y; R_x, R_y$	$B$	1    -1	1

$C_3(\varepsilon = \exp 2\pi i/3)$			$E$	$C_3^+$	$C_3^-$	$m$ (3)
$A, F, G$	$z^2$	$z, R_z$	$A$	1	1	0
$(B, C), (D, E)$	$(zx, yz), (x^2 - y^2, xy)$	$(x, y), (R_x, R_y)$	$E$	$\begin{Bmatrix} 1 & \varepsilon & \varepsilon^* \\ 1 & \varepsilon^* & \varepsilon \end{Bmatrix}$	$\begin{Bmatrix} 1 \\ 1 \end{Bmatrix}$	$\begin{Bmatrix} 1 \\ 2 \end{Bmatrix}$

$C_4$			$E$	$C_4^+$	$C_2$	$C_4^-$	$m$ (4)
$A$	$z^2$	$z, R_z$	$A$	1	1	1	0
$D, E$	$x^2 - y^2, xy$		$B$	1	-1	1	2
$(B, C), (F, G)$	$(zx, yz)$	$(x, y), (R_x, R_y)$	$E$	$\begin{Bmatrix} 1 & i & -1 & -i \\ 1 & -i & -1 & i \end{Bmatrix}$	$\begin{Bmatrix} 1 \\ 1 \end{Bmatrix}$	$\begin{Bmatrix} 1 \\ 1 \end{Bmatrix}$	$\begin{Bmatrix} 1 \\ -1 \end{Bmatrix}$

$C_6(\varepsilon = \exp 2\pi i/6)$			$E$	$C_6^+$	$C_3^+$	$C_2$	$C_3^-$	$C_6^-$	$m$ (6)
$A$	$z^2$	$z, R_z$	$A$	1	1	1	1	1	0
$F, G$			$B$	1	-1	1	-1	1	3
$(B, C)$	$(zx, yz)$	$(x, y), (R_x, R_y)$	$E_1$	$\begin{Bmatrix} 1 & \varepsilon & -\varepsilon^* \\ 1 & \varepsilon^* & -\varepsilon \end{Bmatrix}$	$\begin{Bmatrix} -1 \\ -1 \end{Bmatrix}$	$\begin{Bmatrix} -\varepsilon \\ -\varepsilon^* \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon^* \\ \varepsilon \end{Bmatrix}$	$\begin{Bmatrix} 1 \\ -1 \end{Bmatrix}$	$\begin{Bmatrix} 1 \\ -1 \end{Bmatrix}$
$(D, E)$	$(x^2 - y^2, xy)$		$E_2$	$\begin{Bmatrix} 1 & -\varepsilon & -\varepsilon^* \\ 1 & -\varepsilon^* & -\varepsilon \end{Bmatrix}$	$\begin{Bmatrix} 1 \\ 1 \end{Bmatrix}$	$\begin{Bmatrix} -\varepsilon \\ -\varepsilon^* \end{Bmatrix}$	$\begin{Bmatrix} -\varepsilon^* \\ -\varepsilon \end{Bmatrix}$	$\begin{Bmatrix} -2 \\ 2 \end{Bmatrix}$	$\begin{Bmatrix} -2 \\ 2 \end{Bmatrix}$

TABLE XVIII  
THE GROUPS  $S_n$  ( $n = 2, 4, 6$ )

$S_2(C_i)$			$E$	$i$	$I$	
$A, B, C, D, E, F, G$	$z^2, zx, yz, x^2 - y^2, xy$	$R_x, R_y, R_z$	$A_g$	1	1	0
		$x, y, z$	$A_u$	1	-1	1

$S_4$			$E$	$S_4^+$	$C_2$	$S_4^-$	$l$	$m$ (4)		
$D, E$	$z^2$	$R_z$	$A$	1	1	1	1	0	0	
	$x^2 - y^2, xy$							3	2	
$A$		$z$	$B$	1	-1	1	-1	2	2	
	$(zx, yz)$							1	0	
$(B, C), (F, G)$		$(x, y), (R_x, R_y)$	$E$	$\begin{cases} 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & 1 \end{cases}$	1	-1	-1	1	2	-1
					1	-1	-1	1	1	
					2	1			2	1
					1	-1			1	-1

$$S_6 \equiv C_{3i} = C_3 \times C_2$$

TABLE XIX  
THE GROUPS  $C_{nh}$  ( $n = 1, 2, 3, 4, 6$ )

$C_{1h}(C_s)$				$E$	$\sigma_h$	$l$	$m$ (2)
$B,C,F,G$	$z^2, x^2 - y^2, xy$	$x, y, R_z$	$A'$	1	1	0	0
						1	1
$A,D,E$	$zx, yz$	$z, R_x, R_y$	$A''$	1	-1	2	1
						1	0

The  $x$ - and  $y$ -axes lie in the  $\sigma_h$ -plane

$$C_{2h} = C_2 \times C_i$$

$C_{3h}(\epsilon = \exp 2\pi i/3)$			$E$	$C_3^+$	$C_3^-$	$\sigma_h$	$S_3^+$	$S_3^-$	$l$	$m$ (6)
$F, G$	$z^2$	$R_z$	$A'$	1	1	1	1	1	0	0
									3	3
$A$		$z$	$A''$	1	1	1	-1	-1	4	3
									1	0
$(B, C)$	$(x^2 - y^2, xy)$	$(x, y)$	$E'$	$\begin{cases} 1 & \epsilon & \epsilon^* & 1 & \epsilon & \epsilon^* \\ 1 & \epsilon^* & \epsilon & 1 & \epsilon^* & \epsilon \end{cases}$	2	-2	1	1	2	2
					1	-1	2	1	1	-1
					2	1	3	-2	2	-1
$(D, E)$	$(xz, yz)$	$(R_x, R_y)$	$E''$	$\begin{cases} 1 & \epsilon & \epsilon^* & -1 & -\epsilon & -\epsilon^* \\ 1 & \epsilon^* & \epsilon & -1 & -\epsilon^* & -\epsilon \end{cases}$	3	-2	2	-1	3	2
					2	-1	3	2	3	2
					3	2	3	2	3	2

$$C_{4h} = C_4 \times C_i$$

$$C_{6h} = C_6 \times C_i$$

TABLE XX  
THE GROUPS  $C_{nv}$  ( $n = 2, 3, 4, 6$ )

$C_{2v}$			$E$	$C_2$				$(+2)$	$\phi$
$A, D$	$z^2, x^2 - y^2$	$z$	$A_1$	1	1	1	1	0	$c$
$E$	$xy$	$R_z$	$A_2$	1	1	-1	-1	2	$s$
$B, F$	$xz$	$x, R_y$	$B_1$	1	-1	1	-1	1	$c$
$C, G$	$yz$	$y, R_x$	$B_2$	1	-1	-1	1	1	$s$

The  $x$ - and  $y$ -axes lie in the  $\sigma_v$  and  $\sigma_v'$  planes respectively

$C_{3v}$			$E$	$2C_3$	$3\sigma_v$	$m$ (+6)	$\phi$	
$A$	$z^2$	$z$	$A_1$	1	1	1	0	$c$
$G$				1	1	1	3	$s$
$F$		$R_z$	$A_2$	1	1	-1	3	$c$
				1	1	-1	6	$s$
$(B,C),(D,E)$	$(zx,yz),(x^2-y^2,xy)$	$(x,y),(R_x,R_y)$	$E$	2	-1	0	1,2,4,5	$(c,s)$

The  $y$ -axis lies in one of the  $\sigma_v$  planes

$C_{4v}$			$E$	$C_2$	$2C_4$	$2\sigma_v$	$2\sigma_d$	$m$ (+4)	$\phi$
$A$	$z^2$	$z$	$A_1$	1	1	1	1	0	$c$
		$R_z$	$A_2$	1	1	1	-1	4	$s$
$D$	$x^2 - y^2$		$B_1$	1	1	-1	1	2	$c$
$E$	$xy$		$B_2$	1	1	-1	-1	2	$s$
$(B,C),(F,G)$	$(zx,yz)$	$(x,y),(R_x,R_y)$	$E$	2	-2	0	0	0	$1,3$ $(c,s)$

The  $x$ - and  $y$ -axes lie in the  $\sigma_v$  planes.

$C_{6v}$			$E$	$2C_6$	$2C_3$	$C_2$	$3\sigma_v$	$3\sigma_d$	$m$ (+6)	$\phi$
$A$	$z^2$	$z$	$A_1$	1	1	1	1	1	0	$c$
		$R_z$	$A_2$	1	1	1	-1	-1	6	$s$
$F$			$B_1$	1	-1	1	-1	-1	3	$c$
$G$			$B_2$	1	-1	1	-1	1	3	$s$
$(B,C)$	$(zx,yz)$	$(x,y),(R_x,R_y)$	$E_1$	2	1	-1	-2	0	1,5	$(c,s)$
$(D,E)$	$(x^2-y^2,xy)$		$E_2$	2	-1	-1	2	0	2,4	$(c,s)$

The  $x$ - and  $y$ -axes lie in a  $\sigma_v$  and a  $\sigma_d$  plane respectively.

TABLE XXI  
THE GROUPS  $D_n$  ( $n = 2, 3, 4, 6$ )

$D_3$			$E$	$C_2^x$	$C_2^y$	$C_2^z$	$l$	$m$ (+2)	$\phi$
$E$	$z^3, x^2 - y^2$	$A_1$	1	1	1	1	0	0	$c$
							3	2	$s$
$A, D$	$xy$	$z, R_z$	1	1	-1	-1	2	2	$s$
							1	0	$c$
$C, G$	$yz$	$y, R_y$	1	-1	1	-1	2	1	$c$
							1	1	$s$
$B, F$	$xz$	$x, R_x$	1	-1	-1	1	2	1	$s$
							1	1	$c$

The  $x$ -,  $y$ -, and  $z$  axes coincide with the three  $C_2$ -axes

$D_3$		$E$	$2C_3$	$3C_2'$	$l$	$m$ (+3)	$\phi$
$G$	$x^2$	$A_1$	1	1	1	0 3	0 3 $c$ $s$
$A, F$	$z, R_z$	$A_2$	1	1	-1	4 1	3 0 $s$ $c$
$(B, C), (D, E)$	$(zx, yz), (x^2 - y^2, xy)$	$(x, y), (R_x, R_y)$	$E$	2	-1	0	1, 2 $(c, s)$

The  $y$ -axis coincides with one of the  $C_2'$  axes

D <sub>4</sub>			E	C <sub>2</sub>	2C <sub>4</sub>	2C <sub>2</sub> '	2C <sub>2</sub> ''	l	m (+4)	φ
A	z <sup>2</sup>	A <sub>1</sub>	1	1	1	1	1	0	0	c
			5	4	s					
	z, R <sub>z</sub>	A <sub>2</sub>	1	1	1	-1	-1	4	4	s
		1	0	c						
E	x <sup>2</sup> - y <sup>2</sup>	B <sub>1</sub>	1	1	-1	1	-1	2	2	c
			3	2	s					
D	xy	B <sub>2</sub>	1	1	-1	-1	1	2	2	s
			3	2	c					
(B,C),(F,G)	(zx,yz)	(x,y),(R <sub>x</sub> ,R <sub>y</sub> )	E	2	-2	0	0	0	1,3	(c,s)

The  $x$ - and  $y$ -axes coincide with the two  $C_2'$ -axes.

$D_6$			$E$	$2C_6$	$2C_3$	$C_2$	$3C_2'$	$3C_2''$	$I$	$m$ (+6)	$\phi$
	$z^2$		$A_1$	1	1	1	1	1	1	0 7	0 6 $c$ $s$
$A$		$z, R_z$	$A_2$	1	1	1	1	-1	-1	6 1	6 0 $s$ $c$
$F$			$B_1$	1	-1	1	-1	1	-1	4 3	3 3 $s$ $c$
$G$			$B_2$	1	-1	1	-1	-1	1	4 3	3 3 $c$ $s$
$(B,C)$	$(zx, yz)$	$(x, y), (R_x, R_y)$	$E_1$	2	1	-1	-2	0	0		1,5 $(c,s)$
$(D,E)$	$(x^2 - y^2, xy)$		$E_2$	2	-1	-1	2	0	0		2,4 $(c,s)$

The  $x$ - and  $y$ -axes coincide with a  $C_2'$ - and a  $C_2''$ -axis respectively.

TABLE XXII  
THE  $D_{nd}$  GROUPS ( $n = 2, 3$ )

$D_{2d}$			$E$	$C_2$	$2S_4$	$2C_2'$	$2\sigma_d$	$I$	$m$ (+4)	$\phi$
$E$	$z^2$		$A_1$	1	1	1	1	1	0 3	0 2 $c$ $s$
$D$		$R_z$	$A_2$	1	1	1	-1	-1	4 3	4 2 $s$ $c$
	$x^2 - y^2$		$B_1$	1	1	-1	1	-1	2 5	2 4 $c$ $s$
$A$	$xy$	$z$	$B_2$	1	1	-1	-1	1	2 1	2 0 $s$ $c$
$(B,C), (F,G)$	$(zx, yz)$	$(x, y), (R_x, R_y)$	$E$	2	-2	0	0	0		1,3 $(c,s)$

The  $x$ - and  $y$ -axes coincide with the two  $C_2'$ -axes.

$$D_{3d} = D_3 \times C_i$$



TABLE XXIII  
THE  $D_{nh}$  GROUPS ( $n = 2, 3, 4, 6$ )

$$D_{2h} = D_2 \times C_i$$

$D_{3h}$			$E$	$2C_3$	$3C_2'$	$\sigma_h$	$2S_6$	$3\sigma_v$	$I$	$m$ (+6)	$\phi$	
$F$	$z^2$	$A_1'$	1	1	1	1	1	1	0	0	$c$	
									3	3	$c$	
$G$	$R_z$	$A_2'$	1	1	-1	1	1	-1	6	6	$s$	
									3	3	$s$	
$A$	$z$	$A_1''$	1	1	1	-1	-1	-1	4	3	$s$	
									7	6	$s$	
		$A_2''$	1	1	-1	-1	-1	1	4	3	$c$	
									1	0	$c$	
$(B,C)$	$(x^2 - y^2, xy)$	$(x, y)$	$E'$	2	-1	0	2	-1	0	2	2,4	$(c,s)$
									1	1,5	$(c,s)$	
$(D,E)$	$(zx, yz)$	$(R_x, R_y)$	$E''$	2	-1	0	-2	1	0	2	1,5	$(c,s)$
									3	2,4	$(c,s)$	

The  $x$ -axis coincides with a  $C_2'$ -axis

$$D_{4h} = D_4 \times C_i$$

$$D_{6h} = D_6 \times C_i$$

TABLE XXIV  
THE CUBIC GROUPS<sup>a</sup>

$T(\varepsilon = \exp (2 \pi i / 3))$			$E$	$4 C_3^{+}$	$4 C_3^{-}$	$3 C_2$	$I$	$m$ (2)	$\phi$
$E$			$A$	1	1	1	1		
	$(x^2 - y^2, z^2)$		$E$	$\begin{Bmatrix} 1 \\ 1 \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon \\ \varepsilon^* \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon^* \\ \varepsilon \end{Bmatrix}$	$\begin{Bmatrix} 1 \\ 1 \end{Bmatrix}$		
								2	2
$(A, F, G), (D, B, C)$	$(xy, zx, yz)$	$(x, y, z); (R_x, R_y, R_z)$	$T$	3	0	0	-1	1	0
									$c$
								1	$(c, s)$

$$T_h = T \times C_i$$

0			<i>E</i>	$8C_3$	$3C_2$	$6C_4$	$6C_2'$
<i>E</i>	$(x^2 - y^2, z^2)$	$(x, y, z), (R_x, R_y, R_z)$	$A_1$	1	1	1	1
			$A_2$	1	1	1	-1
			<i>E</i>	2	-1	2	0
			$T_1$	3	0	-1	1
			$T_2$	3	0	-1	-1
$(A, 6B - F, 6C + G)$							
$(D, 10B + F, 10C - G)$	$(xy, zx, yz)$						

$$O_h = 0 \times C_i$$

$T_d$			$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$F$			$A_1$	1	1	1	1
			$A_2$	1	1	1	-1
	$(x^2 - y^2, z^2)$		$E$	2	-1	2	0
$(D, 10B + F, 10C - G)$		$(R_x, R_y, R_z)$	$T_1$	3	0	-1	1
$(A, 6B - F, 6C + G)$	$(xy, zx, yz)$	$(x, y, z)$	$T_2$	3	0	-1	-1

<sup>a</sup> In all cases  $x$ ,  $y$ , and  $z$  coincide with the three  $C_2$ -axes, and hence with the fourfold axes also, when they exist





# 3. Chemical Binding

C. A. Coulson and J. T. Lewis

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## 1. General Principles

### 1.1 The Nature of the Problem

At first sight the application of quantum theory to chemical problems seems to be a very attractive prospect. For the accurate prediction of reaction rates and the calculation of molecular properties such as size and shape would be of enormous practical value. Indeed, if sufficiently reliable calculations were to become possible, much of the exploratory experimental work which consumes so much of a chemist's time would become unnecessary. No one would now seriously dispute that the behaviour of the electrons and nuclei, on which these chemical properties depend, are accurately described by quantum mechanics, in its present form. This is because any new fundamental changes in the framework of the theory which may ultimately become necessary in order to account for the behaviour of elementary particles and high energy phenomena, are most unlikely to affect the conclusions of the theory on the atomic level. Yet, despite the attractiveness of the project, we are very far from achieving the goal outlined above. The reason for this is partly a lack of sufficiently powerful mathematical techniques to handle the wave equation with more than very few particles, but where this number is not yet large enough (as in a metal) to permit the use of statistical methods. But perhaps an even graver handicap is a conceptual one: chemistry is built around certain concepts, such as that of valence and the chemical bond. Yet there is not so far a sufficient correlation between these concepts and the techniques which are available. Since these techniques are so important, both for solving the wave equation and for correlating with experimental concepts, we shall devote the first section of this chapter to a discussion of them, leaving the applications to the second section.

The problem which we want to solve is quite simply stated. But even a glance at it will show how difficult it is. A stable molecule consists of electrons in rapid motion about a number of nuclei, while these nuclei themselves execute a more ponderous oscillatory motion around their mean positions. If it were possible to calculate the total energy  $E$  for all positions of the nuclei, then we could determine what these mean positions were, and so predict both the lengths of the bonds between them, and the valence angles between these bonds. But this is not easy, as the following example shows. The molecule of methane — the gas which bubbles up from the decaying vegetation at the bed of a river — is known to have the chemical formula  $\text{CH}_4$ ; it is also known to be tetrahedral in character, with the central carbon atom surrounded nearly symmetrically by the four hydrogen atoms. There are 10 electrons, giving us a total of 15 moving particles. The

Schrödinger wave equation, from which the energy must be calculated, is a partial differential equation in 45 independent variables. It is true, as we shall show later in this section, that certain symmetry properties can be made to reduce the number of independent variables very substantially. But it is equally true that the problem will even then present exceedingly grave difficulties if we desire an accurate value for the energy. Yet, as we shall see, any discussion of why the molecule is stable against splitting up into pieces, or why the HCH bond angles are approximately all equal to the tetrahedral angle  $109^{\circ}28'$ , or why the C-H distance is nearly 1.1 Å, must depend on as accurate as possible a value of the energy.

In general terms; given  $N$  specified nuclei and  $n$  electrons, what are the stable mean configurations (if any) of the nuclei? How much energy is required to pass from one configuration of the nuclei to some other? What are the wave functions for the various states of the system? What are the cross sections for the various rearrangement collisions which are possible between two such systems, and which correspond to chemical reactions? These are the essential problems in chemical binding.

### 1.2 The Born-Oppenheimer Approximation

Fortunately there is one simplification of this general problem, which has more hope of leading to a solution. This is arrived at by realising that the much greater mass of the nuclei compared with the electrons makes their motion far slower and less extensive (Chapter 4, § 1, in this volume). In the Born-Oppenheimer approximation we ask what are the wave functions and energy levels for the  $n$  electrons when all the  $N$  nuclei are held fixed. The great advantage in this separation of electronic and nuclear motions lies in the fact that if we are able to calculate the electronic energy for all positions of the nuclei, then we can subsequently discuss the motion of these nuclei (i.e., the molecular vibrations). The potential energy for this motion is just the electronic energy defined in this way. Finally we can allow for the small interaction between the two motions as a small perturbation. In practice, however, it is not often possible to determine the electronic energy for arbitrary positions of the nuclei in more complex molecules than diatomic ones, and we are therefore frequently reduced to supposing that the nuclei are held fixed at their observed mutual positions in the ground state.

### 1.3 The Variation Method

In all that follows we shall confine ourselves to the problem of finding the wave functions and energy levels of a system consisting of  $n$  electrons

moving in the field of  $N$  fixed nuclei. Even this problem is difficult, and the only cases for which it has satisfactorily been solved are the one-electron diatomic molecules (Vol. I, Chapter 3, § 6.3). Almost without exception the approximation methods employed, both for these and other more complicated molecules, rely on the variation method (Vol. I, Chapter 6). But in making use of this method we take advantage of the result — itself a direct consequence of the postulates of the quantum theory — that if two dynamical variables commute then there exists a set of functions which are simultaneously eigenfunctions of both dynamical variables (Vol. I, Chapter 2, § 3.3). Since we are chiefly concerned with the energy, our first step will be to construct trial functions which not only satisfy the conditions of the variational theorem, but also are eigenfunctions of operators which commute with the Hamiltonian. If we can find sufficiently many such operators this will considerably simplify our choice of trial function; but even then we cannot be sure of getting a good approximation to the energy. Much effort has been directed towards devising trial functions which, in addition to satisfying the symmetry and other conditions just mentioned, manage to incorporate chemical intuition and the results of previous experience with other molecules. Several of these will be described in the second part of this chapter.

### 1.4 Electron Distributions

In addition to the electronic energy, one of the most fundamental needs is to know the electron distribution. This can easily be obtained once the wave function has been obtained. For many purposes we can think of the molecule as if it consisted of the given nuclei imbedded in a cloud of negative charge density due to the electrons. Not all electron distributions are permitted, but only those which are determined by the Schrödinger equation and the Pauli Exclusion Principle. It is important to realize that it is only via the Schrödinger equation that wave mechanics enters the calculation of molecular energies. Despite the statements that are sometimes made, there are no “mysterious quantum-mechanical forces” involved in holding the atoms of a molecule together. There is a theorem — the Hellmann-Feynman theorem<sup>1</sup> — which shows that if we are given the electron density distribution, then the forces acting on the nuclei are just those calculated by a straightforward “classical” electrostatical interaction between the charge density and the nuclei, in which each element of charge exerts the usual inverse square law force on every other element.

There is one important property of the molecular charge clouds which may be mentioned here, and which points to one of the major difficulties



in molecular calculations. Charge distributions which have a high electron concentration between the nuclei tend to be more binding than those without. This is quite evident from the contour diagrams for the electron density in the various states of  $H_2^+$ , where detailed and accurate calculations can be made (Vol. I, Chapter 3, § 6.3). It is well illustrated in Fig. 1, which shows the

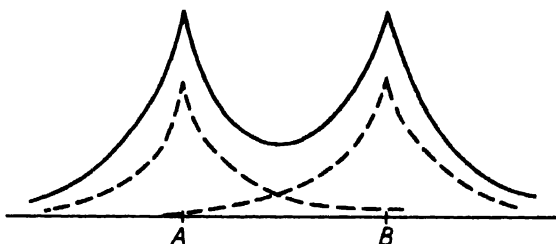


FIG. 1. The full line represents the charge density in the ground state of  $H_2^+$  at points along the axis. The two broken lines each represent half the density of an isolated electron around each nucleus.

density in the ground state of  $H_2^+$  for points along the axis. Between the nuclei it is clear that the charge density is distinctly greater than the sum of the densities associated with half the electron around each nucleus, and in the  $1s$  atomic level.

A very general explanation of this may be given, as follows. Suppose (Fig. 2) that we bring up two atoms A and B, each with their separate charge clouds, and at first (Fig. 2a) we merely superpose their charge densities.

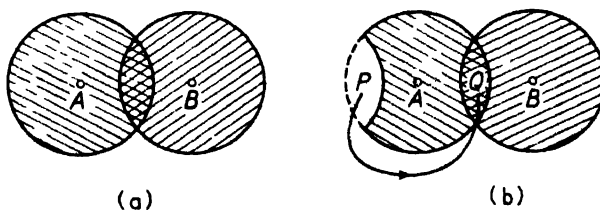


FIG. 2. (a) The superposition of two spherically symmetrical charge distributions is represented symbolically. Charge moved from P to Q has the same potential energy relative to A but the energy relative to B is lowered.

Now (Fig. 2b) let us move some charge from the region around P to the region around Q. This will not alter the potential energy relative to nucleus A, but it will lower the potential energy relative to nucleus B. This

will therefore tend to give greater stability to the combination of A and B. In terms of the Hellmann-Feynman theorem we may say that this additional charge, being negative, attracts both A and B towards it, and hence serves to hold the nuclei together. Our conclusion is that we ought to move a certain amount of charge from the farther parts of the molecule into the region between the nuclei. Of course, if we put too much charge there, we shall (a) reduce the effective volume over which the electrons move and thus reduce their mean de Broglie wavelength and increase their kinetic energy: and (b) increase the mutual repulsive potential energy  $e^2/r_{ij}$  between each pair of electrons  $i$  and  $j$ . It is as a result of these factors that the actual numerical build-up of charge, though quite definite, is not large, being of the order of 0.1 to 0.5  $e$ .

This discussion shows how critical is the electron-electron interaction term  $e^2/r_{ij}$ . Yet this also points to a situation where molecular calculations are more difficult than atomic ones. This is because the build-up occurs *between* the nuclei, and is not associated with either the one or the other. At very least it becomes clear that the evaluation of the contribution which  $e^2/r_{ij}$  makes to the energy is going to involve us in some peculiarly difficult integrals. Much of this will appear in § 2.

### 1.5 The Hamiltonian of the Molecule

For any system of  $n$  electrons each of mass  $m$  the classical nonrelativistic Hamiltonian is

$$H = \sum_{i=1}^n \frac{\mathbf{p}_i^2}{2m} + V \quad (1)$$

where  $\mathbf{p}_i$  is the momentum of the  $i$ th electron, and  $V$  is the total potential energy. This is the sum of nucleus-electron attraction terms, electron-electron repulsion terms and nucleus-nucleus repulsion terms.

Thus

$$V = \sum_{\substack{\alpha=1 \\ \alpha > \beta}}^N \sum_{\beta=1}^N \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} e^2 - \sum_{i=1}^n \sum_{\alpha=1}^N \frac{Z_\alpha}{r_{i\alpha}} e^2 + \sum_{\substack{i=1 \\ i > j}}^n \sum_{j=1}^n \frac{e^2}{r_{ij}}, \quad (2)$$

where  $Z_\alpha$  is the positive charge on nucleus  $\alpha$  whose position vector is  $\mathbf{R}_\alpha$ ,

$$R_{\alpha\beta} = |\mathbf{R}_\alpha - \mathbf{R}_\beta|, \quad r_{i\alpha} = |\mathbf{R}_\alpha - \mathbf{r}_i|, \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \quad (3)$$

and  $\mathbf{r}_i$  is the position vector of the  $i$ th electron. This leads to the Schrödinger wave equation

$$\frac{\hbar^2}{2m} \sum_i \nabla_i^2 \Psi + \left[ E_{\text{tot}} - e^2 \left\{ \sum_{\alpha > \beta} \sum \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} - \sum_i \sum_{\alpha} \frac{Z_\alpha}{r_{i\alpha}} + \sum_{i,j} \sum \frac{1}{r_{ij}} \right\} \right] \Psi = 0. \quad (4)$$

The eigenvalues  $E_{\text{tot}}$  of this equation give the total electronic energy of the allowed states, and depend parametrically on the  $R_{\alpha\beta}$  which describe the relative positions of the nuclei. The nuclear repulsion term  $\sum \sum_{\alpha > \beta} (Z_\alpha Z_\beta / R_{\alpha\beta}) e^2$  is independent of the electron coordinates. It is usual, therefore, to leave out this term and work with the purely electronic wave equation

$$\frac{\hbar^2}{2m} \sum_i \nabla_i^2 \Psi + \left[ E - e^2 \left\{ \sum_{i,j} \sum \frac{1}{r_{ij}} - \sum \sum \right\} \right] \Psi = 0. \quad (5)$$

It will then follow that

$$E \equiv E(R_{\alpha\beta}, \dots) = E_{\text{tot}} - e^2 \sum_{\alpha > \beta} \sum \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \quad (6)$$

It is important, before going further, to remind ourselves of the approximations involved in (5). These are of three kinds: (1) fixed nucleus hypothesis, (2) neglect of relativistic effects, and (3) assumption of point nuclei.

In the first of these we have effectively neglected all coupling between the electronic and nuclear motions.

In the second approximation it is not easy to say just how serious our assumption is, since we do not even know how to write down the relativistic Hamiltonian for more than one particle. We may hope that the one-particle case will give a reasonable indication of the nature of the neglected terms. These must, at very least, include the relativistic change of mass with velocity, spin-spin and spin-orbit interaction. The relativistic change of mass is allowed for if we write the kinetic energy as

$$\sqrt{(m^2 c^4 + \mathbf{p}^2 c^2)} \quad (7)$$

instead of  $\mathbf{p}^2/2m$ , as in (1). This change alone leads to a modification of (5) known as the Klein-Gordon equation. It applies to particles (e.g.,  $\pi^-$  meson) which has no spin. If we expand (7) in the form

$$mc^2 + \mathbf{p}^2/2m - \frac{\mathbf{p}^4}{8m^3 c^2} \quad (7a)$$

we see that the chief alteration is the addition of the constant rest mass energy  $mc^2$  and a relatively small correction term  $-\mathbf{p}^4/8m^3 c^2$ . This would be the correct way to deal with mesonic molecules, in which the electron is

replaced by a  $\pi^-$  meson. But the correct formula for dealing with electrons arises from a generalization of the Dirac equation for the electron (Vol. III, Chapter 1). This leads to the more complicated expression<sup>2</sup> for one electron in a potential field  $V$

$$H = \frac{\mathbf{p}^2}{2m} + V - \frac{\mathbf{p}^4}{8m^3c^2} - \frac{\hbar^2}{4m^2c^2} (\text{grad } V) \cdot \text{grad} + \frac{\hbar}{2m^2c^2} \mathbf{S} \cdot [\text{grad } V \times \mathbf{p}] \quad (8)$$

when  $\mathbf{S} = \frac{1}{2}\hbar\boldsymbol{\sigma}$  is the spin angular momentum of the electron. The first three terms will be recognized from (1) and (7a); the last term is the spin-orbit term arising from the interaction of the intrinsic magnetic moment of the electron with the magnetic moment produced by its motion. (Since it is charged its motion in an orbit corresponds to a tiny current loop and therefore an equivalent magnetic moment.) Both it and the spin-orbit term will be large only when  $\text{grad } V$  is large; that is, close to nuclei with large charge  $Z$ . But the mass term in  $\mathbf{p}^4$  will also be large only when the electron has high velocity, i.e., close to nuclei with large  $Z$ . It can be shown that, for an atom, the last three terms in (8) lead to a first-order energy change proportional to  $Z^4/c^2$ . On account of the  $Z^4$  dependence, these terms will be unimportant for small  $Z$  (e.g., below  $A\frac{1}{2}$  for which  $Z = 13$ ), but above this value there is some evidence that their total effect is much larger. On the other hand, since their effect is most noticeable near the nuclei, and these are the places where the charge cloud is least affected by molecule formation, it seems reasonable that their effect on the energy of a molecule is closely equal to the sum of their effects on the separate atoms of the molecule. Thus these terms, together with certain others such as spin-other orbit and spin-other spin which concern the interaction between the spin of one electron and the orbital and spin magnetic moments of another electron, are most unlikely to have any serious influence on the calculation of binding energy in a molecule. There is, however, one other effect of the single electron spin-orbit term which we shall have to consider later, when discussing the various operators which commute with the Hamiltonian.

Our third approximation in (5) lies in the assumption that the nuclei are structureless points. This is not the case. On the one hand since the nucleus possesses a finite size the potential energy formula  $e^2 Z_\alpha / r_{i\alpha}$  must break down when the electron is sufficiently close to the nucleus. Since nuclear radii are only of order  $10^{-13}$  cm, and atomic and molecular sizes are of orders  $10^{-8}$  cm, their effect is usually exceedingly small. But the internal structure of a nucleus may lead to its possessing electric and magnetic multipole moments. It can be shown<sup>8</sup> that a nucleus cannot

manifest an electric dipole moment, but provided that its total internal angular momentum  $I$  is at least unity (in terms of  $\hbar$ ) it can have a non-vanishing electric quadrupole moment. In a nonuniform electric field, there will be  $2I + 1$  possible orientations of the axis of  $I$ , giving rise to a fine structure superimposed on the electronic energy levels of the molecule. Transitions among these levels give rise to radiation of low energy, lying in the radiofrequency range with typical wavelengths in the range of 30 metres to 30 cm. Now it will often happen that the electron distribution in a molecule will give rise to a nonvanishing field gradient at one or more nuclei. Consequently from a study of the long wave absorption we can sometimes get information about the distribution of the electrons<sup>4</sup> In addition to this, if  $I$  is not zero the nucleus may possess a magnetic dipole moment. Such a moment, if placed in a powerful magnetic field, will have energy levels depending on the  $2I + 1$  possible orientations of the axis of  $I$  with respect to this field. Once again, transitions between these is associated with radiation in the radiofrequency range. Now suppose that a molecule with one such nucleus is placed in a constant external magnetic field. This field will induce small currents among the valence electrons and these, in their turn, will partly screen the nucleus from the full effect of the external field. When the same nucleus is placed in different molecules the screening will differ, and hence the wavelengths of absorption. These so-called chemical shifts are small, but in careful nuclear magnetic resonance experiments they may be measured very accurately, and provide useful information about the charge distribution in a molecule.<sup>5</sup> It will be recognized that both this latter nuclear magnetic resonance and the earlier quadrupole coupling measurements, each provide us with one piece of information about the distribution of charge. Neither of them gives us the detailed charge, in the same sort of way as electron diffraction and X-ray scattering can do. But they can nevertheless provide exceedingly useful checks on other conclusions made on other grounds.

Having discussed the approximations involved in our molecular Hamiltonian, we may now return to (5). If we introduce atomic units this may be written

$$H\Psi \equiv \left( -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i>j} \sum \frac{1}{r_{ij}} - \sum_i \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} \right) \Psi = E\Psi. \quad (9)$$

Our next task is to look for operators which commute with this Hamiltonian, so that we can then proceed to label the eigenvalues of  $H$ . In view of what we said in § 1.3 each such operator will be associated with one particular quantum number.

### 1.6 Symmetry Properties of the Hamiltonian

In atomic problems the total orbital angular momentum operator  $L^2$  and also the three components  $L_x, L_y, L_z$  all commute with  $H$ , and play a fundamental role in labelling the eigenvalues of  $H$ . Let us therefore look at the commutator of  $L_z$  with  $H$ , where  $H = -\frac{1}{2}\Sigma V_k^2 + V$ . Since the total angular momentum  $\mathbf{L}$  is the sum of the individual momenta,

$$\mathbf{L} = -i \sum_k \mathbf{r}_k \times \nabla_k \quad (11)^*$$

therefore

$$\begin{aligned} [L_z, H] &= [L_z, V] \\ &= -i \sum_k [(\mathbf{r}_k \times \nabla_k)_z V - V(\mathbf{r}_k \times \nabla_k)_z] \\ &= -i \sum_k (\mathbf{r}_k \times \nabla_k V)_z \end{aligned} \quad (12)$$

(remembering that the result of operating with the product of two operators is defined to be the result of operating with each successively.) Now if  $V$  is spherically symmetrical  $\nabla_k V$  is directed radially, and (12) vanishes, whatever the direction of the  $z$ -axis. This is the case of the atom. But if  $V$  is not spherically symmetrical (12) will vanish only if  $V$  has axial symmetry, and  $z$  is taken along this axis. This is the case of the linear molecule. With the atom all three components of  $L$  commute with  $H$  and so therefore does  $L^2$ . With the linear molecule the component  $L_z$  along the axis commutes with  $H$ , but  $L_x, L_y$ , and  $L^2$  do not. This shows clearly how much we lose in the way of symmetry when we pass from an atom to a molecule. With the linear molecule the eigenvalues of  $L_z$  are integers, denoted by  $A = 0, \pm 1, \pm 2, \dots$  and they may be used to label the eigenvalues of  $H$ . When  $|A| = 0, 1, 2, \dots$  we call the states  $\Sigma, \Pi, \Delta, \dots$  states, by analogy with the use of  $S, P, D, \dots$  for atomic states (Chapter 1). Similarly, by analogy with the notation using small letters  $s, p, d, \dots$  for individual atomic electrons, we shall have  $\sigma, \pi, \delta, \dots$  for individual molecular electrons.

If we had included the spin-orbit term (the last term in (8)) in the Hamiltonian, the above argument would have broken down completely. But, once again by analogy with the atomic situation, it can be saved by the

\* The symbol  $i$  here means  $\sqrt{-1}$ , and should not be confused with the numbering of the electrons.

use of the total angular momentum  $\mathbf{J}$  in place of the total orbital angular momentum  $\mathbf{L}$ .  $\mathbf{J}$  is the sum of the total intrinsic (spin) angular momentum  $\mathbf{S}$ , and the orbital momentum  $\mathbf{L}$ .

$$\mathbf{J} = \mathbf{L} + \mathbf{S}, \quad (13)$$

where

$$\mathbf{S} = \sum \mathbf{s}_k$$

The argument is now the same as before except that  $J_z$  replaces  $L_z$ . However, unless the molecule contains a nucleus with large  $Z$ , this modification is not usually necessary, except when we are considering certain electronic transitions which would be forbidden if it were not for the spin-orbit interaction. The phosphorescence of many organic molecules is of this "singlet-triplet" kind.

We have seen that in linear molecules  $L_z$  (or  $J_z$ ) commutes with  $H$  and gives rise to a classification of the electronic states in terms of the quantum number  $\Lambda$ . It is natural to ask whether there is any other type of classification which would apply to the greater number of polyatomic molecules, which do not have axial symmetry. In the absence of such symmetry there is no component of angular momentum which commutes with  $H$ , and so is a constant of the motion. But it may happen that the nuclear framework possesses some kind of symmetry. If so, this may be used to classify the eigenfunctions of the Hamiltonian. An example is the water molecule  $\text{H}_2\text{O}$ , which is known to be triangular in shape. With the notation of Fig. 3, let  $C_2$  denote the operation of rotating the axes through  $180^\circ$  around  $Oz$ . This merely shifts one hydrogen atom into the other, and leaves the Hamiltonian invariant. So also does  $\sigma_v$ , defined as reflection in the plane  $\text{HOH}$ ; and so does reflection in the  $yz$ -plane. Only two of these are actually independent, since it can be seen that reflection in  $yz$  is identical with a combination of  $\sigma_v$  and  $C_2$ . This means that there are two effective symmetry operations which leave  $H$  invariant, and so which commute with it.

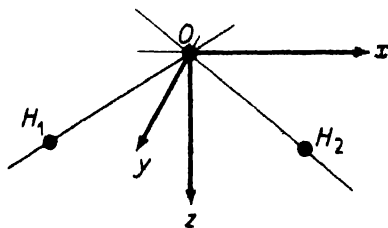


FIG. 3  $\text{H}_2\text{O}$ . The two hydrogen nuclei and the oxygen nucleus all lie in the  $xz$ -plane.

In general let us suppose that the classical Hamiltonian (which is a function of the coordinates of the various electrons) is invariant under some

coordinate transformations. Then the quantum Hamiltonian operator will commute with the operator corresponding to the coordinate transformation. The set of all such transformation operators which commute with the Hamiltonian is called the Schrödinger group of the Hamiltonian. Then the eigenfunctions of the Hamiltonian may be classified according to the irreducible representations of its Schrödinger group. Since the linearly independent eigenfunctions corresponding to the same energy eigenvalue transform into linear combinations of one another under operations of the group they form a basis for a representation of the group. In almost every case the representation is irreducible; but if two irreducible representations have the same energy eigenvalue they are said to be accidentally degenerate. Such accidental degeneracy is not common, but we shall come upon a few examples later (§ 1.10). In the absence of accidental degeneracy the linearly independent eigenfunctions corresponding to the same energy eigenvalue generate an irreducible representation of the Schrödinger group; the dimension of this representation is then the degree of degeneracy of the energy level. Thus information about the possible degrees of degeneracy in any situation can be found from the structure of the corresponding Schrödinger group (Chapter 2, in this volume § 3.4).

Now the possible dimensions  $l_i$  of the irreducible representations of a group are known to be related to the order  $h$  of the group in the following way:

$$l_1^2 + l_2^2 + \dots + l_k^2 = h. \quad (14)$$

In an Abelian group, where all the operations commute with each other,  $h = h$ , so that all the irreducible representations are one-dimensional. Hence, apart from any case of accidental degeneracy, if all the transformation operators which commute with a given Hamiltonian commute with each other, all its energy eigenvalues are nondegenerate. In order that degeneracy of this type shall occur (called symmetry degeneracy to distinguish it from the previous accidental degeneracy) it is necessary to have at least one pair of transformation operators which commute with  $H$ , but not with each other.

The states of a molecule may thus be labelled according to their symmetry: that is, according to the irreducible representation of the Schrödinger group generated by the particular set of linearly independent eigenfunctions of the given energy level. One-dimensional representations are usually denoted by the letters  $A$ ,  $B$ ; two-dimensional ones by  $E$ , and three-dimensional ones by  $T$ . The symbol  $A$  is used for those one-dimensional representations corresponding to functions which are symmetric with respect to rotations about the axis of highest symmetry; the symbol  $B$  refers to those which are antisymmetric. If the functions are symmetric with respect to a reflec-



tion  $\sigma_h$  (where the suffix  $h$  denotes a plane at right angles to the axis of greatest symmetry), one prime ' is attached to the letter denoting the representation; if antisymmetric, two primes '' are attached. Symmetric and antisymmetric functions with respect to inversion in a centre of symmetry are distinguished by a subscript  $u$  or  $g$ , which are short for ungerade (odd) and gerade (even) respectively. Furthermore just as for the case of axial symmetry, large letters, e.g.  $A, E, \dots$  are used for the states of the complete molecule, and small letters, for example,  $a, e, \dots$ , for the symmetry properties of individual electrons.

### 1.7 The Case of the Benzene Molecule $C_6H_6$

All this technique for classifying the states of a molecule will become clear if we consider an example. The benzene molecule is known, both from X-ray and spectroscopic evidence, to be planar in its ground state (Fig. 4) with the six carbon atoms lying at the vertices of a regular hexagon, and the six C-H directions pointing symmetrically outwards. Thus the symmetry properties of the Hamiltonian are those of a molecule with  $D_{6h}$ , since any transformation belonging to this group leaves the molecule unchanged. This group has 24 independent elements, with eight one-dimensional irreducible representations and four two-dimensional ones.

(As a check; using (14),  $8 \times 1^2 + 4 \times 2^2 = 24$ ) These are denoted by  $A_1', A_2', A_1'', A_2'', B_1', B_2', B_1'', B_2'', E_1', E_2', E_1'', E_2''$ . Consider for example the nondegenerate state  $A_2''$ . Since this is of type  $A$ , the wave function must be symmetric for rotations around the axis of greatest symmetry, here the sixfold axis through the centre of the molecule perpendicular to the molecular plane. Since there are two primes '' the function is antisymmetric with respect to reflection in the plane of the molecule. Similarly  $B_1'$  is a nondegenerate state with an eigenfunction which is antisymmetric with respect to rotations about the sixfold axis, but symmetric with respect to reflections in the plane. On the other hand  $E_1''$  is a doubly degenerate level for which both of the two linearly independent wave functions are antisymmetric with respect to reflection in the plane.

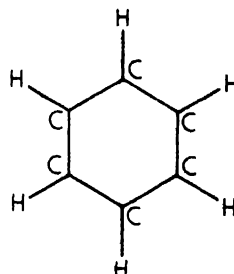


FIG. 4.  $C_6H_6$ . The carbon nuclei lie at the vertices of a regular hexagon and the hydrogen nuclei at those of a circumscribing one.

1.8 More Group Theory:  $C_{\infty v}$ 

This treatment of group symmetry for polyatomic molecules seems at first sight to be quite distinct from the relatively simple  $\Lambda$ -classification for diatomic and other linear molecules, which was based on the component of angular momentum  $L_z$ . However this  $\Lambda$ -classification can be translated into similar language to that used in the previous group theory discussion. This helps us to see that fundamentally the two classifications are analogous. The explanation of this unexpected result may be found by noticing that the operator  $L_z$  may be viewed as the operator corresponding to an infinitesimal rotation of the coordinates about the  $z$ -axis. Thus since in operator terms, with a single electron

$$L_z = \frac{\hbar}{2\pi i} \frac{\partial}{\partial \phi},$$

where  $\phi$  is an azimuthal angle around the symmetry axis, therefore the wave function for this electron with quantum number  $\Lambda$  will vary with  $\phi$  in the same way as  $e^{i\Lambda\phi}$ . Thus a rotation around the axis through an angle  $\phi$  will multiply the wave function by  $e^{i\Lambda\phi}$ . If there are more electrons than one, the same result holds, by summation. Let us denote by  $C_\phi$  the operator corresponding to rotation through this angle  $\phi$ . Then, evidently,

$$C_{\phi_1} \cdot C_{\phi_2} = C_{\phi_1 + \phi_2}. \quad (15)$$

In order to relate  $C_\phi$  to the operator  $L_z$  we recall that a function  $f(A)$  of an operator  $A$  with eigenvalues  $a_n$  and corresponding eigenfunctions  $\psi_n$  is defined as the operator with eigenvalues  $f(a_n)$  and the same eigenfunctions  $\psi_n$ . Now if  $\psi$  is an eigenfunction of  $L_z$  with eigenvalue  $\Lambda$ , then

$$L_z \psi_\Lambda = \hbar \Lambda \psi_\Lambda. \quad (16)$$

So

$$\exp\left(\frac{i}{\hbar} \phi L_z\right) \cdot \psi_\Lambda = e^{i\Lambda\phi} \psi_\Lambda. \quad (17)$$

This means that we may make the identification

$$C_\phi = \exp\left(\frac{i}{\hbar} \phi L_z\right). \quad (18)$$

It is evident that  $C_\phi C_\phi^*$  is the unit operator, so that  $C_\phi$  is unitary.

It follows from (15) that the operations  $C_\phi$  together with their inverses  $C_{-\phi}$  and the identity  $E$  obviously form a group. This is denoted by  $C_{\infty v}$ . It differs in an important respect from the groups considered in Chapter 2

in this volume: it is not of finite order, since the parameter  $\phi$  can take any value within the continuous range 0 to  $2\pi$ . Thus it is an example of a very important class of groups, the finite continuous groups. These are groups in which the elements depend continuously on a finite number of parameters. Summation over the elements of the group now becomes integration over these parameters, and an invariant measure  $d\tau_G$  may be defined as the element of integration. (There is no difficulty in the integration provided that  $\int d\tau_G$  is finite, as in this case.) Thus the fundamental formulas (19) and (20) for the representatives  $D$  and the characters  $\chi$ :

$$\sum_{R \in G} D_{ik}^{(\alpha)}(R) D_{lm}^{(\beta)}(R) = \frac{h}{l_\alpha} \delta_{\alpha\beta} \delta_{il} \delta_{km} \quad (19)$$

where  $l_\alpha$  is the dimension of the representation, and

$$\sum_{R \in G} \chi^\alpha(R) \chi^\beta(R) = h \delta_{\alpha\beta} \quad (20)$$

are replaced by (21) and (22):

$$\int_G D_{ik}^{(\alpha)} D_{lm}^{(\beta)} d\tau_G = \frac{1}{l_\alpha} \int_G d\tau_G \cdot \delta_{\alpha\beta} \delta_{il} \delta_{km}, \quad (21)$$

$$\int_G \chi^{(\alpha)} \chi^{(\beta)} d\tau_G = \int_G d\tau_G \cdot \delta_{\alpha\beta}. \quad (22)$$

Let us consider the special case of  $C_\infty$ . This may, of course, be thought of as the limit of  $C_n$  as  $n \rightarrow \infty$ . Then  $d\tau_G = d\phi$  and so

$$\int_0^{2\pi} d\tau_G = 2\pi. \quad (23)$$

An important case arises when in addition to  $C_\infty$  there is symmetry for reflection  $\sigma_v$  in a plane through the symmetry axis. This leads to  $C_{\infty v}$ , by far the most common of the continuous groups. It applies to all heteronuclear diatomic molecules. Its irreducible representations are easily obtained. Thus, if  $A = 0$ , the wave function is unchanged on rotation through an angle  $\phi$ , and we get the two one-dimensional representations  $A_1$  and  $A_2$ , where  $A_1$  is symmetrical and  $A_2$  is antisymmetrical in the operation  $\sigma_v$ . We label these states  $\Sigma^+$  and  $\Sigma^-$ . If  $A \neq 0$  we have pairs of degenerate functions

$$\psi_\pm = \sqrt{\frac{1}{2\pi}} e^{\pm iA\phi} \quad (24)$$

which give rise to an infinite number of two-dimensional representations. Using

$$C_\phi \psi_\pm = e^{\pm iA\phi} \psi_\pm \quad (25)$$

it is easily seen that

$$\chi(C_\phi) = e^{+iA\phi} + e^{-iA\phi} = 2 \cos A\phi. \quad (26)$$

Thus the character table is

TABLE I  
CHARACTER TABLE FOR  $C_{\infty v}$

$C_{\infty v}$	$E$	$2C_\phi$	$\infty \sigma_v$
$\Sigma^+ A_1$	1	1	1
$\Sigma^- A_2$	1	1	-1
$\Pi E_1$	2	$2 \cos \phi$	0
$\Delta E_2$	2	$2 \cos 2\phi$	0
$E_A$	2	$2 \cos A\phi$	0

It is not difficult to extend this to deal with the case of homonuclear diatomics. We have merely to add inversion in the origin. If we call this operation  $i$  then the new group  $D_{\infty h}$  is

$$D_{\infty h} = C_{\infty v} \times C_i. \quad (27)$$

This allows us to calculate its character table readily enough (Table II).

TABLE II  
CHARACTER TABLE FOR  $D_{\infty h}$

$D_{\infty h}$	$E$	$2C_\phi$	$\infty \sigma_v$	$i$	$2iC_\phi$	$\infty i\sigma$
$\Sigma_g^+ A_{1g}$	1	1	1	1	1	1
$\Sigma_u^+ A_{1u}$	1	1	1	-1	-1	-1
$\Sigma_g^- A_{2g}$	1	1	-1	1	1	-1
$\Sigma_u^- A_{2u}$	1	1	-1	-1	-1	1
$\Pi_g E_{1g}$	2	$2 \cos \phi$	0	1	$2 \cos \phi$	0
$\Pi_u E_{1u}$	2	$2 \cos \phi$	0	-1	$-2 \cos \phi$	0
$\Delta_g E_{2g}$	2	$2 \cos 2\phi$	0	1	$2 \cos 2\phi$	0
$\Delta_u E_{2u}$	2	$2 \cos 2\phi$	0	-1	$-2 \cos 2\phi$	0
		etc.				

On the left-hand side of these two tables for  $C_{\infty v}$  and  $D_{\infty h}$  we have given first the designation of the state in the usual notation for diatomic molecules. This is followed by the designation of the corresponding irreducible representation in the standard group theory notation.

In all the above work we have been dealing with rotation and reflection operators. But these do not exhaust the possible symmetry operations associated with a molecule. Thus a free molecular system is also invariant with respect to the operations which simultaneously permute all the coordinates of equivalent particles, so that the corresponding operators commute with the Hamiltonian. These permutation operators form a unitary group. Now we know that for electrons and other particles with spin  $\frac{1}{2}$ , the Pauli Principle only permits eigenfunctions which are antisymmetric in all the particles. For particles with zero spin the eigenfunctions must be symmetric. In this chapter we are confining our attention to Hamiltonians which do not contain the spin variables explicitly. For these it must be possible to write the total wave function as a simple product of an eigenfunction representing the spin and another representing the space coordinates. In such a case the condition of antisymmetry would require that if the space part is symmetric, the spin part be antisymmetric, and vice versa. But we do not propose to describe the construction of spin eigenfunctions, since this has already been done in relation to complex atoms, and the treatment applies without modification to molecules.

### 1.9 The Jahn-Teller Effect

Our discussion so far has been quite general. By that we mean that we have made no attempt to obtain approximate solutions of the Schrödinger equation, but have used symmetry properties of the Hamiltonian to describe the behaviour of such solutions under various coordinate transformations. In this way we gain insight into the nature of these solutions, as it is imposed by the symmetry of the problem. But before leaving this type of enquiry in order to deal with approximate solutions for the wave functions and energies of molecular systems, we must consider two more of the properties of these functions which can be deduced using the general methods of our preceding paragraphs.

The first of these relates to the fact that in their equilibrium configuration certain types of molecule do not have the most symmetrical shape possible. It might be supposed that molecules would normally tend to seek positions of the greatest symmetry. But, as Jahn and Teller showed,<sup>6</sup> this is not by any means always the case. For if the electronic state is degenerate, symmetric configurations of the nuclei (other than collinear ones) are unstable. The degeneracy considered here is orbital degeneracy, and has nothing to do with the spin. It will be remembered that in this chapter we are only considering spin-free Hamiltonians. The essential point of the present argument is that if the nuclei are moved from a position of greatest symmetry,

this distortion of the nuclear framework will split the previous degeneracy: and in general one or more of the former levels will be lowered, and one or more raised. Thus there must be at least one way in which the molecule may be deformed, and the total energy lowered. Hence the most stable configuration cannot be the symmetrical one. We can put this more precisely by expanding the Hamiltonian  $H$  for one configuration of the nuclei in a Taylor series about a slightly different one. Thus, if  $\mathbf{q}$  denotes a vector whose components are the parameters specifying the configuration of the nuclei (so that  $\mathbf{q}$  is a many-dimensional vector in which  $\mathbf{q} = 0$  denotes the starting symmetrical configuration) then

$$H(\mathbf{q}) = H(0) + (\text{grad } H)_{\mathbf{q}=0} \cdot \mathbf{q} + O(q^2).$$

Now if  $H(\mathbf{q})$  and  $H(0)$  are invariant under a given symmetry group, so is  $H(\mathbf{q}) - H(0)$  and therefore so also are the individual terms in the above expansion. This is because the separate terms are linearly independent. In particular  $(\text{grad } H)_{\mathbf{q}=0} \cdot \mathbf{q}$  is invariant under operations of the given symmetry group. Now let us take the parameters  $\mathbf{q}$  to be the normal vibrational coordinates, and denote them, as usual, by  $\mathbf{Q}$ . The normal coordinates corresponding to a given normal mode generate an irreducible representation of the group. In a formal sense we may regard the  $\mathbf{Q}$  as unchanged, and the coefficients  $(\text{grad } H)_{\mathbf{q}=0}$  as generating the same representation.

Consider now a degenerate electronic level  $E_i(0)$  of  $H(0)$ , for which the eigenfunctions are  $\Psi_{i\sigma}$  ( $\sigma = 1, 2, \dots$ ). Suppose that these eigenfunctions span an irreducible representation  $D_i$  of the group. We shall now show that the configuration of greatest symmetry  $\mathbf{Q} = 0$  cannot be stable. If it were stable it would imply that  $E_i(\mathbf{Q})$  would not contain any terms linear in  $\mathbf{Q}$ . Thus the first-order perturbation energy got by diagonalising  $(\text{grad } H)_{\mathbf{q}=0} \cdot \mathbf{Q}$  with respect to the  $\psi_{i\sigma}$  would all vanish, i.e., the matrix elements

$$\int \psi_{i\sigma} (\text{grad } H)_{\mathbf{q}=0} \psi_{i\rho} d\tau \quad (28)$$

must vanish for all  $\sigma, \rho$ . Now consider a displacement of the nuclei transforming according to the irreducible representation  $D_j$  of the group. The matrix elements will vanish provided that the product  $D_i \times D_j$  does not contain  $D_i$ . If  $D_i \times D_j$  does contain  $D_i$ , then (apart from an exceptional accident) the matrix elements will not vanish. But if the group is a discrete point group and  $D_i$  is not one-dimensional (that is,  $E_i(0)$  is degenerate), then  $D_i \times D_i$  is sure to contain some  $D_j$ , other than the totally symmetric representation. Hence, for this displacement  $D_j$ , the integrals do not vanish,

and there must be a linear term in the variation of the energy with displacement. The symmetrical configuration for the molecule cannot therefore be a stable one.

A particular example of the use of this theorem is to the methane molecule  $\text{CH}_4$  (Fig. 5). If the molecule is tetrahedral, as in the figure, then the ground state of the neutral system has symmetry  $A_{1g}$ , and since there is then no degeneracy, no problem arises. But it may be shown that there are electronically excited states in which one electron has been excited from a  $t_u$  orbital to an  $a_{1g}$  orbital, leading to total symmetry  $T_u$ . Now there is threefold degeneracy, and so these excited states must depart from tetrahedral symmetry, for there must be at least one type of deformation which lowers the energy. It will be noticed that although this type of group theory argument can tell us which types of symmetry are not allowed by the Jahn-Teller effect, and can add information about the possible deformations that would lead to lower energy when the degeneracy is split, it cannot tell us which of the possible deformations actually occurs, nor how large it is. These questions would have to be answered by other means.

This Jahn-Teller argument would break down for the continuous point groups. Hence collinear degenerate configurations are not covered by the theory. For example, a distortion perpendicular to the molecular axis will contain a factor  $e^{i\phi} \pm e^{-i\phi}$ , which will have nonzero matrix components only between states for which  $|\Delta\Lambda| = 1$ . Now if two states of a linear molecule are orbitally degenerate they must have components of angular momentum  $+\Lambda$  and  $-\Lambda$ , where  $\Lambda > 0$ . For these two states  $|\Delta\Lambda| = 2\Lambda$  so that all the matrix components (28) will vanish. Hence collinear configurations may be stable, even when they are degenerate.

### 1.10 The Non-crossing Rule

The second property of molecular energy levels which may be derived from general considerations is the so-called "noncrossing rule." For diatomic molecules, in which each of the energy values  $E$ , depends only on

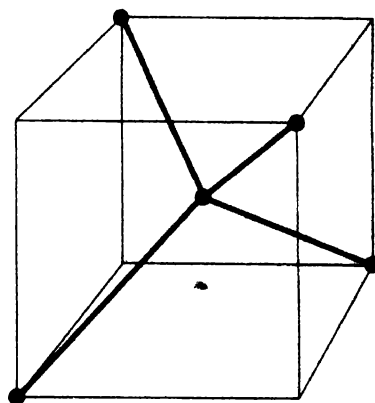


FIG. 5.  $\text{CH}_4$  The carbon nucleus lies at the centre of a regular tetrahedron with the hydrogen nuclei at its vertices.

the internuclear distance  $R$ , so that  $E = E_i(R)$ , it may be stated thus: terms of like symmetry do not cross. That is to say, if we plot the curves corresponding to  $E = E_i(R)$  for all  $i$ , then  $[E_i(R) - E_j(R)]$  has a zero within the range  $0 < R < \infty$  only if  $i$  and  $j$  are states which correspond to different irreducible representations of the symmetry group of the system.

A simple proof is due to Teller.<sup>8</sup> Let  $H(R)$  be the Hamiltonian for a diatomic molecule of which all the eigenfunctions but two are supposed to be known. Take two functions  $\psi_1, \psi_2$  which are orthogonal to all the known eigenfunctions; the two unknown eigenfunctions must be linear combinations of  $\psi_1$  and  $\psi_2$ . We may suppose that  $\psi_1$  and  $\psi_2$  are mutually orthogonal, since if they are not we may replace  $\psi_2$  by a new function  $\psi_2' = \psi_2 + k\psi_1$  and choose  $k$  so that  $\psi_2'$  is orthogonal to  $\psi_1$ . The two unknown eigenvalues  $E_1(R)$  and  $E_2(R)$  are obtained by diagonalizing  $H(R)$  with respect to  $\psi_1$  and  $\psi_2$ . They are the roots of the secular equation

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0,$$

where

$$H_{ij} = \int \psi_i^* H \psi_j d\tau = H_{ji}^*.$$

So

$$E_{1,2} = \frac{H_{11} + H_{22}}{2} \pm \left[ \left( \frac{H_{11} - H_{22}}{2} \right)^2 + |H_{12}|^2 \right]^{1/2}$$

In order that  $E_1(R) = E_2(R)$  should be zero it is necessary and sufficient that  $H_{12}(R)$  and  $H_{11}(R) - H_{22}(R)$  should vanish for the same value of  $R$ . Let us choose a value of  $R$  for which  $H_{11}(R) = H_{22}(R)$ . It would then be a remarkable accident (but nothing more!) if  $H_{12}(R)$  should also vanish for this  $R$ , unless  $H_{12}(R)$  was identically zero on grounds of symmetry. Now  $H_{12}(R)$  will be zero for all  $R$  if  $\psi_1$  and  $\psi_2$  belong to different irreducible representations of the symmetry group of  $H$ , but not otherwise (except by accident). We are justified, therefore, in concluding that, in general, states of different symmetry do not cross. The extension of this argument to other than diatomic molecules is quite straightforward: the only difference is that now  $H_{11} - H_{22}$  and  $H_{12}$  must vanish simultaneously for certain values of all the parameters that are needed to define the relative positions of the nuclei.

The hydrogen molecule ion  $H_2^+$  is an exception to the above noncrossing rule. It is sometimes stated that in  $H_2^+$  this occurs because the wave equation is separable (in spheroidal coordinates; see Section 2). This is to



restate the problem rather than to solve it. It is natural to look for some additional symmetry operation that will commute with  $H(R)$  and so lead to a constant of the motion. With the single electron system of  $H_2^+$  there is such a constant of the motion. But this case is so unique and the particular constant has so little physical significance that it is not worth detailed discussion here.

## 2. Applications

### 2.1 The Simplest Molecular Problem: $H_2^+$

The symmetry considerations which we have developed in the earlier parts of this chapter may now be utilized in constructing approximations to the wave functions for some simple molecules. We consider first the hydrogen molecule ion  $H_2^+$ . This is chosen for two reasons. It is the simplest of all molecules, and, being a one-electron system, its wave function and energy may be determined to any desired accuracy by numerical integration of the Schrödinger equation (Vol. I, Chapter 3, § 6.3). This means that approximate methods may be tried out on  $H_2^+$  and their results compared with the accurate ones. In this way we may judge the likely validity of approximate methods for more complicated molecules for which accurate wave functions cannot be obtained. But  $H_2^+$  is also the prototype for all homonuclear diatomic molecules in the same way that the hydrogen atom is the prototype for all other atoms.

The Hamiltonian for  $H_2^+$  may be taken to be

$$H = -\frac{1}{2} \nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} \quad (29)$$

where, in the notation of Fig. 6,  $P$  is the single electron and  $A, B$  are the two nuclei. This Hamiltonian has the symmetry of the group  $D_{\infty h}$ .

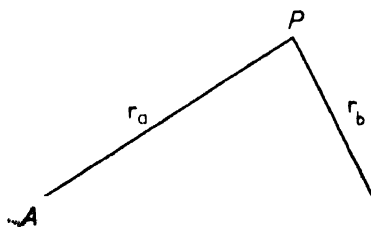


FIG. 6.  $H_2^+$ : notation.

Now if we keep the proton at  $A$  fixed, and move  $B$  further and further away, the electron will be around either the one or the other nucleus, and in either case the energy levels will tend closer and closer to those of an isolated hydrogen atom. We might therefore be tempted to consider the  $H_2^+$  molecule as if it were a hydrogen atom (at  $A$ , say) perturbed by the presence of a unit positive charge at  $B$ . We could then set up some sort of trial function for  $\psi$  and use the variational theorem to estimate the energy. For

example, we could take  $\psi$  to be simply the normal 1s hydrogen atom function

$$\psi = \phi_A = \sqrt{\frac{1}{\pi}} e^{-r_a} \quad (30)$$

But a moment's reflection will soon show us that we could not expect great success with such a trial function. This is because the function (30) behaves correctly under the coordinate transformations  $C_\phi$  and  $\sigma_v$  of  $D_{\infty h}$ , but not under  $i$ , where  $i$  represents inversion in the midpoint of AB. Under the operation  $i$ ,  $\phi_A$  goes into

$$\phi_B = \sqrt{\frac{1}{\pi}} e^{-r_b}.$$

However the functions

$$\chi_g = N_g(\phi_A + \phi_B) \quad (31a)$$

$$\chi_u = N_u(\phi_A - \phi_B) \quad (31b)$$

do have correct symmetry, as shown by the subscripts  $g$  and  $u$ , and are suitable for use as trial functions. The numerical factors  $N_{g,u}$  are chosen to normalize  $\chi_{g,u}$  and are given by

$$N_{g,u} = [2(1 \pm S)]^{-1/2} \quad (32)$$

where

$$S = \int \phi_A \phi_B d\tau,$$

and the  $+$  sign corresponds to  $N_g$ . Since  $\phi_A$  and  $\phi_B$  are purely real, so is  $S$  and hence  $\psi_g$  and  $\psi_u$  are also real.

There is a simple physical interpretation of (31a, b). For large values of  $R$  we have seen that the system tends towards an isolated hydrogen atom. The electron may be either around A, giving  $\phi_A$ , or around B, giving  $\phi_B$ . We do not know which of these it will choose, and must therefore consider both, leading to a wave function  $c_1\phi_A + c_2\phi_B$ . By symmetry these two possibilities must occur with equal weight, so that  $c_1^2 = c_2^2$ . Thus  $c_1 = \pm c_2$  and we are led once more to the functions  $\chi_g$  and  $\chi_u$  of (31).

It is instructive — though in this simple case, unnecessary — to look at this procedure in terms of the projection operators defined in Chapter 2, § 5.3 of this volume. The operator corresponding to the inversion transformation  $i$  is denoted by  $i$ , so that

$$\phi_B = i\phi_A, \quad \phi_A = i\phi_B. \quad (33)$$

Now  $\phi_A$  may be looked upon as being composed of two parts, one of gerade symmetry and the other ungerade. For we can write

$$\begin{aligned}\phi_A &= \frac{1}{2}(\phi_A + \phi_B) + \frac{1}{2}(\phi_A - \phi_B) \\ &= \frac{1}{2}(1 + i)\phi_A + \frac{1}{2}(1 - i)\phi_A \\ &= P_g \phi_A + P_u \phi_A\end{aligned}\quad (34)$$

where  $P_{g,u}$  are the projection operators

$$P_{g,u} = \frac{1}{2}(1 \pm i). \quad (35)$$

These are projection operators because, for example

$$P_g^2 = \frac{1}{4}(1 + i)^2 = \frac{1}{4}(1 + 2i + i^2) = \frac{1}{4}(2 + 2i) = P_g.$$

The reader should verify that the expressions (35) may be arrived at by using the relevant formulas of Chapter 2 and the character table of the group  $C_i$ . (Since we are concerned only with the operation  $i$  we do not need to consider the full group  $D_{\infty h}$ , but merely  $C_i$ .)

The function  $\chi_g$  provides an approximation to the lowest  ${}^2\Sigma_g$  state of  $H_2^+$ , and  $\chi_u$  to the lowest  ${}^2\Sigma_u$  state. The details of the calculation of the energy with these functions has been described in Vol. I, Chapter 6, § 3.1 and we do not need to repeat it here. But we may notice that when we include the nuclear repulsion term  $1/R$ , the total energy curve of the  ${}^2\Sigma_g$  state shows a minimum at about  $R = 2a_0$ , whereas that of  ${}^2\Sigma_u$  shows no minimum. The two energy curves are described as attractive and repulsive respectively, and the corresponding orbitals are called bonding and antibonding. To justify these names we ought, strictly, to show that the same situation occurs when, instead of the approximate  $\chi_{g,u}$ , we use the accurate ones. Fortunately this is so. Reference to the properties of the wave functions for these states, given in Vol. I, Chapter 3, § 6, shows that for the bonding orbital there is an increase in the electron probability density between the nuclei, but that for the antibonding orbital there is a decrease. Thus by the Feynman theorem of § 1.4 we should expect forces on the nuclei, due to the electronic distribution, of such a kind as to make the bonding state more stable than the antibonding. The designations as bonding and antibonding are therefore sensible ones.

The trial functions (31) have no flexibility. But they may be improved by introducing a variable parameter in  $\phi_A$  and  $\phi_B$ . For example we could put

$$\phi_A = \sqrt{\left(\frac{Z^3}{\pi}\right)} e^{-Zr}. \quad (36)$$

instead of (30).  $Z$  is the so-called effective nuclear charge, since (36) is the atomic orbital for a nuclear charge  $+Z$  units. It is also called the "orbital

exponent" of the atomic orbital — a designation that may easily be extended to more complicated functions, if necessary. In our case  $Z$  may be regarded as a parameter, whose optimum value, at any  $R$ , may be determined by using the wave functions (31) and choosing  $Z$  so as to minimize the energy integral

$$E(Z;R) = \int \psi^* H \psi d\tau. \quad (37)$$

The variation of  $Z$  with  $R$  will be different for the g and u states. The two functions  $Z_{g,u}(R)$  found in this way are shown in Fig. 7. As might be

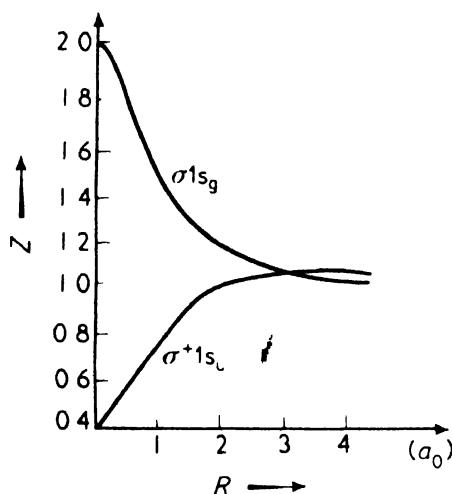


FIG. 7. The effective nuclear charge for the two lowest states of  $H_2^+$  (C. A. Coulson, *Trans Faraday Soc.* **33**, 1479 (1937))

expected, both  $Z$  values tend to unity as  $R$  goes to infinity. At the observed equilibrium distance, which is almost correctly predicted by this wave function, the effective nuclear charge is found to be 1.24 for the bonding orbital  $\chi_g$ .

There is a simple physical explanation of this enhanced effective nuclear charge. For (see Fig. 6) where there are two nuclei instead of merely one, the solitary electron is pulled more powerfully towards the molecule. The size of the electron cloud will therefore be reduced (the "volume" occupied by the charge-cloud in  $H_2^+$  is much less than in H). This is represented by a larger  $Z$  value, since then the function  $e^{-Zr}$  falls off more rapidly with  $r$ .

Further improvement could be made by making  $\phi_A$  still more flexible, while yet retaining the necessary molecular symmetry in  $\psi$ . For example, when the electron is near to nucleus A, it is also being pulled towards B.

So we might anticipate that  $\phi_A$  should not be spherically symmetrical, as in (30) and (36), but should contain some angular terms. This could be achieved by taking a sum of hydrogenlike atomic orbitals such as those of the  $2p, 3p, 3d, \dots$  states. All such orbitals could be considered, provided only that they all have the quantum number  $m = 0$  since we are constructing a trial function for a  $\Sigma$  state. These additional terms would correspond to a polarization distortion of the original  $1s$  atomic orbitals. In fact it is found by experience that simply adding a  $2p_{m=0}$  function gives a great improvement<sup>9</sup> and brings the calculated energy close to the true value (0.5996 instead of 0.6026 atomic units). Dickinson used a  $\phi$  of the form (not normalized)

$$\phi_A = e^{-Zr_a} + cz_a e^{-Zr_a} \quad (38)$$

where the  $z$ -axis lies along the line of centres, and  $c$  and  $Z$  are variable parameters found by the variation method. The optimum value of  $c$  varies with  $R$ , but tends to zero both for large and small  $R$ .

## 2.2 Separated Atom and United Atom Viewpoints

The calculations for  $H_2^+$  just described are based upon what is now called the separated atom viewpoint. This means that we choose our orbitals as linear combinations of atomic orbitals (for short, the LCAO approximation) and relate these orbitals to the situation that would arise if the two nuclei were separated by an infinite distance. Every state of  $H_2^+$ , whether ground state or excited state, must dissociate into defined states of the two component nuclei and the electron. We use these atomic orbitals as the basis of our variational trial function, modifying them if necessary by the introduction of effective nuclear charges and polarization. But we could have started at the other extreme, with the nuclei brought so close that they become coincident. In the case of the ground state of  $H_2^+$ , this would pass over into the  $1s$ -state of the helium ion  $He^+$ . This could be called the united atom. It has nuclear charge  $Z = 2$ . So our first approximation to a united atom wave function for  $H_2^+$  would be simply

$$\psi_g = \left( \frac{2^3}{\pi} \right)^{1/2} e^{-2r} \quad (39)$$

where  $r$  is now measured from the mid point  $O$  of  $AB$ . There is one immediate objection to such a wave function. It has a discontinuity of slope when  $r = 0$ . This is entirely appropriate to an atom, for the  $1s$  orbital should have such a discontinuity at the nucleus. With  $H_2^+$  of course, there should be two discontinuities at  $A$  and  $B$ , but none at  $O$ . Thus the results using (39) will

not be so good as with (31). They could be improved by smoothing the function at O, if we took a sufficient number of atomic orbitals around O, and varied their coefficients in an LCAO wave function. Experience shows, however, that a large number of such terms are needed, so that the calculation is not very easy to handle.

But this does not imply that the idea of a correlation diagram which relates the molecular function to its two extremes — the united atom and the separated atom — is without value. It is exceedingly useful in understanding the nature of the molecular orbitals (such as 31), and providing insight into the way that the total charge distribution in the molecule is built up. A correlation diagram of this kind for homonuclear diatomics (such as  $H_2$ ,  $Li_2$ ,  $O_2$ ) is shown in Fig 8. This diagram illustrates very nicely

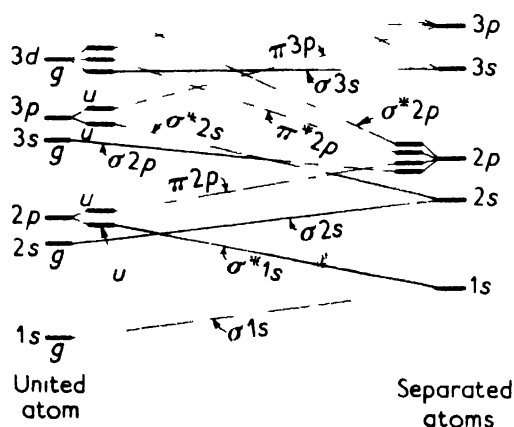


FIG. 8. Correlation diagram for homonuclear diatomic molecules.

the noncrossing rule of § 1.10. Thus levels of similar symmetry cannot cross. Further, since the u,g property is constant along any such correlation curve, we can see that the united atom description may require higher principal quantum numbers than the separated atom description. (This has sometimes been called promotion.) An example is the  ${}^2\Sigma_u$  level of  $H_2^+$  for which the separated atom description is  $\phi_A - \phi_B$  with  $\phi_A$  the 1s orbital around nucleus A. The lowest u-state in  $He^+$  is the  $2pz$  level, and so the united atom wave function for this state would have the form

$$\psi_u = Nr \cos \theta e^{-r} \quad (40)$$

where  $N$  is a normalizing factor.

Despite this difficulty the united atom approximation has been developed very successfully for the excited electronic states. This is to be expected, for we know that with a single hydrogen atom the mean size of the charge cloud increases as the square of the principal quantum number  $n$ . If, for example,  $n = 3$ , the mean size is 9 times as great as for the ground state. With the molecule this means that almost all the charge cloud lies well outside the region AB, so that the electron "sees" a positive charge near the centre of the molecule which is not very different from that of the united atom. The most satisfactory procedure seems to be to write down the united atom wave function, as in (39) and (40), and then replace  $r$  by  $\lambda R/2$ , and  $\cos \theta$  by  $\mu$ , where

$$\lambda = (r_a + r_b)/R, \quad \mu = (r_a - r_b)/R. \quad (41)$$

Since  $\lambda R/2 \rightarrow r$  and  $\mu \rightarrow \cos \theta$  as  $R \rightarrow 0$  these functions have the correct form at  $R = 0$ .

Very high accuracy, over a wide range of  $R$  values, can be obtained by using a linear combination of united atom and separated atom type wave functions. But the numerical minimization of the energy integral becomes tedious.

Before leaving the problem of  $H_2^+$  we ought to add that the wave equation is separable in terms of the spheroidal coordinates  $\lambda, \mu, \phi$  where  $\lambda, \mu$  are as in (41) and  $\phi$  is an azimuthal angle around the axis AB. As a result the accurate wave functions are all of the form  $\psi = L(\lambda)M(\mu)\Phi(\phi)$  where,  $L, M, \Phi$  are functions of  $\lambda, \mu, \phi$  respectively. This enables solutions as accurate as we wish to be obtained (Vol. I, Chapter 3, § 6.3). A very good approximate solution at the equilibrium distance  $R = 2a_0$  turns out to be

$$\psi = e^{-a\lambda} (1 + b\mu^2) \quad \text{where } a = 1.35, b = 0.447. \quad (42)$$

### 2.3 The Neutral Hydrogen Molecule $H_2$ : Heitler-London Approximation

The separated atom viewpoint leads fairly obviously in the case of  $H_2^+$  to functions of the form  $\phi_A \pm \phi_B$ . But for the two electron case of  $H_2$  there are two distinct possibilities, which we shall refer to as the Heitler-London and molecular-orbital approximations. We shall discuss them in turn.

In the Heitler-London approximation<sup>10</sup> we notice that when  $R \rightarrow \infty$  the electrons will go to separate nuclei, and the energy will be that of two isolated hydrogen atoms. Thus, analogously to (30), we might take as our starting point the product function  $\phi_A(1)\phi_B(2)$  where, as before

$$\phi_A(1) = \sqrt{\frac{1}{\pi}} e^{-r_{a1}}, \quad \phi_B(2) = \sqrt{\frac{1}{\pi}} e^{-r_{b2}} \quad (43)$$

Such a function has correct symmetry properties under the operations  $C_\phi$  and  $\sigma_v$ , but under inversion  $i$  it goes into  $\phi_B(1)\phi_A(2)$ . Proceeding as before, we apply the projection operators  $P_{g,u}$  and obtain two functions which, when normalized to unity, have the form

$$\psi_{g,u} = N_{g,u} [\phi_A(1)\phi_B(2) \pm \phi_B(1)\phi_A(2)] \quad (44a)$$

with

$$N_{g,u} = [2(1 \pm S^2)]^{-1/2} \quad (44b)$$

and

$$= \int \phi_A(1)\phi_B(2) d\tau. \quad (44c)$$

If the  $\phi$  functions had been complex, we should have taken  $|S|$  instead of  $S$ , where, now,  $S$  would be the integral  $\int \phi_A^*(1)\phi_B(1) d\tau_1$ .

The functions (44) provide trial functions for molecular states  $\Sigma_g, \Sigma_u$ . Since the  $g$  function is symmetric with respect to interchange of the labels 1 and 2 of the electrons, and the  $u$  function is antisymmetric, the Pauli exclusion principle requires that the  $g$  state be a singlet, and the  $u$  state a triplet. The full functions, including spin, would be

$$\Psi_g = \psi_g \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\sqrt{2}, \quad \text{symmetry } {}^1\Sigma_g, \quad (45a)$$

$$\Psi_u = \psi_u \times \frac{\alpha(1)\alpha(2)}{\beta(1)\beta(2)} \frac{i}{[\alpha(1)\beta(2) + \beta(1)\alpha(2)]/\sqrt{2}}, \quad \text{symmetry } {}^3\Sigma_u. \quad (45b)$$

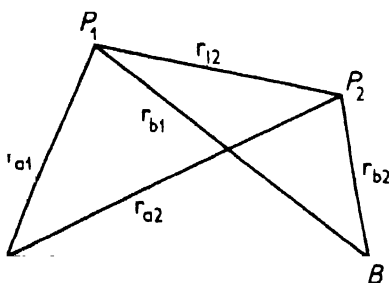


FIG. 9.  $H_2$ : notation.

In (45b) we may take any one of the three spin functions. This shows that the state is a triplet.  $\Psi_g$  of course, is a singlet.

We can regard this method as being based on a particular breakdown of the complete molecular Hamiltonian  $H$  into the sum of two atomic Hamiltonians and an interaction Hamiltonian  $H_{int}$ . Thus, since (see Fig. 9)

$$H = -\frac{\hbar^2}{2} (\nabla_1^2 + \nabla_2^2) - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}} \quad (46)$$

we may write

$$H = H_A(1) + H_B(2) + H_{int} \quad (47)$$



where  $H_A(1)$ ,  $H_B(2)$  are the Hamiltonians for electron 1 around atom A and 2 around B, and where

$$H_{\text{int}} = -\frac{1}{r_{b1}} - \frac{1}{r_{a2}} + \frac{1}{r_{12}}. \quad (48)$$

The point of importance about this breakdown of  $H$  is that

$$[H_A(1) + H_B(2)]\phi_A(1)\phi_B(2) = (E_A + E_B)\phi_A(1)\phi_B(2)$$

where

$$\begin{aligned} H_A(1)\phi_A(1) &= E_A\phi_A(1) \\ H_B(2)\phi_B(2) &= E_B\phi_B(2). \end{aligned} \quad (49)$$

The physical advantage of the subdivision (47) is that it separates the energy of the two atoms from the energy of their interaction. This is a great help since with most molecules the binding energy is only a very small fraction of the total energy.

The Heitler-London method which we have just described is the prototype for the valence-bond method for polyatomic molecules. We shall return to this presently.

#### 2.4 The Hydrogen Molecule $H_2$ : Molecular-Orbital Approximation

There is an alternative method of approximation to the wave function for  $H_2$ . This method is the molecular analogue of the usual "aufbau" principle for atoms. According to the aufbau (i.e., building-up) principle, we build up a trial function for a complex atom out of one-electron atomic orbitals (Chapter 1, § 2.6, and § 13). Our usual designation of the electron distribution in an atom, such as the statement that the lowest state of the carbon atom is  $(1s)^2(2s)^2(2p)^2\ ^3P$  implies that there are certain allowed atomic orbitals labelled as  $1s, 2s, \dots$  and we allot the electrons to these, beginning with the lowest energy and continuing until all our electrons have been accounted for. There is simply no reason why a similar procedure should not be adopted for molecules. In the case of  $H_2$  this method corresponds to a different way of subdividing the Hamiltonian (46). Instead of (47) which leads to the Heitler-London method, let us write

$$H = H^0(1) + H^0(2) + \frac{1}{r_{12}} \quad (50)$$

where

$$H^0(1) = -\frac{1}{2}\nabla_1^2 - \frac{1}{r_{a1}} - \frac{1}{r_{b1}}. \quad (51)$$

The operator  $H^0(1)$  will be recognized as being simply the Hamiltonian for the one-electron molecule ion  $H_2^+$  (cf., Eq. 29). If it were not for the term  $1/r_{12}$  the subdivision (50) would lead to a wave function built up from molecular-orbitals of a bicentric kind. This means that, for the ground state, we should make use of the  $\chi_g$  and  $\chi_u$  defined in (31a, b), and write for our trial function

$$\Psi = \chi_g(1)\chi_g(2) \times \text{spin factor.} \quad (52)$$

With more complex molecules a subdivision of the total Hamiltonian similar to (50) is always possible, and will lead to wave functions which generalize (52) in just the same way that the wave functions for complex atoms generalize the corresponding functions for atomic hydrogen and helium.

According to this method we build our molecular wave function out of molecular orbitals (m.o.'s). Each of these — for the case of a diatomic molecule — will have a definite component of angular momentum around the axis, and may therefore be designated as  $\sigma, \pi, \delta, \dots$  corresponding to  $\Lambda = 0, \pm 1, \pm 2, \dots$ . But we have seen in § 2.1 that there are both bonding and antibonding m.o.'s. It is usual to add an asterisk to the symbol for an antibonding orbital. Thus  $\sigma$  would denote a bonding, and  $\sigma^*$  an antibonding orbital.

Once we have set up our type of wave function, as in (52), we can proceed to introduce flexibility by including parameters, whose values are to be determined by the variation method. The same types of flexibility which we described in § 2.1 can be adapted to this two-electron situation. With sufficient flexibility a very good energy result can be obtained. But even without many variable parameters the results of the m.o. method are closely similar to those of the Heitler-London method. There are certain characteristic differences, as we shall now see, when we come to describe the calculations in rather more detail.

## 2.5 Heitler-London Method for $H_2$ ; Details of Calculation

Let us return to § 2.3 and substitute the wave function (44) in the energy integral

$$= \iint \psi^* H \psi d\tau_1 d\tau_2 \quad (53)$$

using (46)–(49) for the Hamiltonian  $H$ . (Here, as elsewhere in this chapter,  $d\tau_i$  denotes the volume element of the configuration space of electron  $i$ , and the integration is over all configuration space, unless otherwise stated.)

Direct substitution, taking account of the symmetry of two nuclei, leads to the result

$$E_g = 2 E_{1s} + Q_g + \alpha_g \quad (54)$$

$$E_u = 2 E_{1s} + Q_u - \alpha_u \quad (55)$$

where  $E_{1s}$  is the energy of the 1s state of an isolated hydrogen atom, and where

$$Q_g = \frac{J}{1 + S^2}, \quad Q_u = \frac{J}{1 - S^2} \quad (56)$$

$$\alpha_g = \frac{K}{1 + S^2}, \quad \alpha_u = \frac{K}{1 - S^2} \quad (57)$$

$$J = \iint \phi_A^*(1) \phi_B^*(2) \left( \frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} \right) \phi_A(1) \phi_B(2) d\tau_1 d\tau_2 \quad (58)$$

$$K = \iint \phi_A^*(2) \phi_B^*(1) \left( \frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} \right) \phi_A(1) \phi_B(2) d\tau_1 d\tau_2$$

$$S = \int \phi_A^*(1) \phi_B(1) d\tau_1$$

and may be supposed purely real, as in (44c). It will be noticed that  $J$  and  $K$  are matrix components of the interaction operator  $H_{\text{int}}$  of (48).  $J$  is called a Coulomb integral and  $K$  an exchange integral, since in the two halves of the integrand the electrons appear to have exchanged places. Such exchange, of course, is not any sort of physical exchange. It only arises by virtue of the way in which we have split up the complete Hamiltonian (46) into parts, as in (47). In the m.o. method, with a different subdivision of  $H$ , there is usually nothing corresponding precisely to exchange energies. In the Heitler-London method this exchange shows itself in the fact that we cannot use the simple product function  $\phi_A(1)\phi_B(2)$ , but must have the fully symmetrical or antisymmetrical functions (44). If we had decided to use  $\psi = \phi_A(1)\phi_B(2)$ , i.e., if we had neglected exchange, we should have replaced (54)–(59) by

$$E = 2 E_{1s} + J.$$

The functions  $Q$  and  $\alpha$  are sometimes called the Coulomb energy and exchange energy respectively.

If we complete the integrations the Coulomb integral  $J$  reduces to a sum of two terms:

$$J = \iint |\phi_A(1)|^2 \frac{1}{r_{12}} |\phi_B(2)|^2 d\tau_1 d\tau_2 - 2 \int |\phi_A(1)|^2 \frac{1}{r_{b1}} d\tau_1. \quad (60)$$

The first term here is simply the electrostatic repulsion energy between two charge clouds of density  $|\phi_A(1)|^2$  and  $|\phi_B(2)|^2$ . The second is twice the attractive energy of a charge cloud around atom A and a nuclear charge of the opposite sign at B. In exactly the same way the exchange integral  $K$  becomes

$$K = \iint (\phi_A(1)\phi_B^*(1)) \frac{1}{r_{12}} (\phi_A^*(2)\phi_B(2)) d\tau_1 d\tau_2 - 2S \int \phi_A(1)\phi_B^*(1) \frac{1}{r_{b1}} d\tau_1. \quad (61)$$

There is no simple physical interpretation of these terms, though sometimes we speak of the product  $\phi_A(1)\phi_B^*(1)$  as an overlap, or exchange, density, and then there is a parallel between (60) and (61).

The numerical evaluation of the one-electron integrals is achieved without difficulty by transforming the integrand to spheroidal coordinates (41). These involving  $1/r_{12}$  are more difficult. A review of methods of evaluating molecular integrals has been given by Dalgarno.<sup>11</sup>

In order to obtain the total energy of the molecule we must add to the electronic energy the Coulomb repulsion  $1/R$  between the nuclei. In Fig. 10

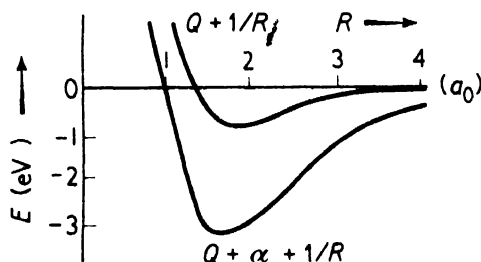


FIG. 10.  $Q + (1/R)$  and  $Q + \alpha + (1/R)$  are plotted against  $R$  for the ground state of  $H_2$ .

both  $Q + 1/R$  and  $Q + \alpha + 1/R$  are plotted as functions of  $R$  for the ground state  $E_g$ . Since the exchange integral  $K$  in (59) turns out to be negative, the energy  $E_g$  in (54) is lower than  $E_u$  in (55). A minimum of the total energy is predicted at a separation of  $R = 0.869$  Å, and the difference  $E(R = \infty) - E(R_{\min})$  is 3.14 eV. This quantity is the binding energy, and should be compared with the observed dissociation energy, suitably corrected for the zero-point vibrational energy of the nuclei, of 4.75 eV.

There are several ways in which we may improve upon the simple Heitler-London calculation, by introducing variable parameters into our

wave functions. First we may introduce an effective nuclear charge in the atomic orbitals, writing

$$\phi_A(i) = \sqrt{\frac{Z^3}{\pi}} e^{-Zr_i}$$

similarly to (36). Wang<sup>12</sup> showed that the optimum  $Z$  varied from 1.6725 at  $R = 0$  (corresponding to a helium atom) down to 1.0 at large  $R$  (see Fig. 11).

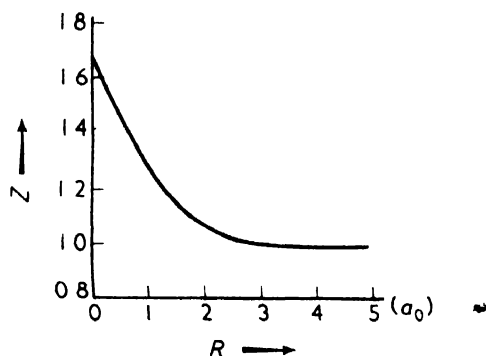


FIG. 11. The effective nuclear charge for the Wang function for  $H_2$  as a function of internuclear distance.

At the calculated equilibrium separation,  $Z = 1.166$ , and the calculated binding energy is 3.76 eV. This represents a substantial improvement over the earlier treatment, particularly in  $R_{\min}$ , which is now estimated to be 0.743 Å, compared with the observed 0.740 Å, but there is still a considerable error in the dissociation energy. The physical explanation of the enhanced value of  $Z$  is much the same as in the discussion of  $H_2^+$  in § 2.1. But like all the concepts that we use in this fashion, it must not be taken too literally, and its precise value depends upon the particular form of the trial function chosen. The proper use of these concepts is to suggest plausible trial functions: after that, they are best forgotten.

A second improvement is to introduce angular dependence in adopting the polarized atomic orbitals of (38). This was used by Rosen<sup>13</sup> who thus raised the calculated dissociation energy to 4.02 eV. Further angular terms, and more flexible radial terms, could be added, but we shall not discuss the details here, since the method itself is perfectly straightforward, though tedious.

## 2.6 Covalent-Ionic Resonance

There is still one further important improvement to be made. In the Heitler-London wave function (44) it was supposed that the wave function was to be built up from functions such that, as  $R \rightarrow \infty$ , one electron went

each nucleus. This equal division of the electrons is sometimes called a valent sharing, and the wave function

$$N[\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)]$$

is called the covalent function, written  $\psi_{\text{cov}}$ . But there are some energy levels of  $\text{H}_2$  which correspond to situations where, as  $R \rightarrow \infty$ , both electrons go to the same nucleus. The molecule then dissociates into  $\text{H}^- + \text{H}^+$ , or  $\text{H} + \text{H}^+ + e$ . There is at least one known bound state of  $\text{H}^-$ , so that we might anticipate functions for  $\text{H}_2$  of the general form

$$\psi_{\text{ion}} = [\chi_A(1,2) \pm \chi_B(1,2)] \times \text{normalizing factor} \quad (62)$$

where  $\chi_A(1,2)$  is some approximate wave function for  $\text{H}^-$ . The simplest such function is

$$\chi_A(1,2) = \phi_A(1)\phi_A(2) \quad (63)$$

where  $\phi_A$  is a hydrogenlike 1s atomic orbital with some effective nuclear charge  $Z'$ . We refer to (62) as an ionic function since, physically, it corresponds to a situation in which both electrons are more likely to be found around the same nucleus. The particular symmetrical and antisymmetrical combinations in (62) are required for precisely the same reasons as in (44).

Now it is easy to verify that neither the covalent nor ionic functions are exact eigenfunctions of the Hamiltonian. We may therefore expect that since both have the same symmetry, we should get an improved trial function by taking a linear combination

$$\psi = \psi_{\text{cov}} + \lambda\psi_{\text{ion}} \quad (64)$$

in which  $\lambda$  is an additional variational parameter. Considerations of this kind led Weinbaum<sup>14</sup> to investigate the ground state of  $\text{H}_2$  with functions of type (64), incorporating both the screening factor  $Z$  of Wang and the polarization term of Rosen. Without the Rosen term the calculated equilibrium bond length was now 0.749 Å and the binding energy 4.00 eV. There were three variable parameters ( $Z, Z', \lambda$ ) for each value of  $R$  considered. In the final calculation incorporating the polarization term,  $R$  was not varied, but the four parameters  $Z, Z', c, \lambda$  were. The calculated binding energy becomes 4.10 eV. This is still a good way below the observed 4.75 eV, and the progressively slower increase as we add more functions suggests that this is about as far as it is worthwhile to proceed along these lines. We could, of course, go on adding more terms. But it is better to organize the whole calculation rather differently, in a way that permits us to introduce our parameters more systematically. We shall refer to one such calculation later, but it would be out of place to do so here, since the method (due to

James and Coolidge) is hardly likely to be applied to much more complicated systems than  $H_2$ . The method of covalent-ionic resonance — as the use of (64) is usually called — can be applied to many and more complicated molecules, and therefore it plays a fundamental role in our descriptions of the bonding in normal molecules.

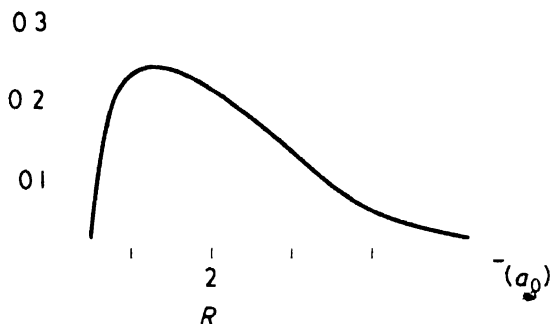


FIG 12. Ionic-covalent resonance in  $H_2$

The variation of  $\lambda$  with  $R$  is shown in Fig. 12,<sup>15</sup> using separately normalized  $\psi_{\text{cov}}$  and  $\psi_{\text{ion}}$  in (64). At the equilibrium distance  $\lambda \approx 1/6$ , and falls rapidly to zero as  $R$  increases.

### 2.7 Molecular-Orbital Function for $H_2$ ; Details of Calculation

We now want to elaborate a little further the m.o. discussion which was started in § 2.4. There we regarded the  $H_2$  molecule as having a wave function built up from one or other of two molecular orbitals,  $\chi_g$  and  $\chi_u$ . According to (31) these are given by the LCAO expressions

$$\chi_g(i) = N_g[\phi_A(i) + \phi_B(i)], \quad \chi_u(i) = N_u[\phi_A(i) - \phi_B(i)]. \quad (65)$$

The resulting wave function (52) is then

$$\Psi = \chi_g(1)\chi_g(2) \times \text{spin factor} \quad (66)$$

where the spin factor is  $[\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\sqrt{2}$ . This method is sometimes referred to as the LCAO-MO method. It is important to realize that the two halves of this description are distinct. Thus we may have a m.o. method without the additional simplification of expressing each m.o. as a linear combination of atomic orbitals such as (65). Indeed this representation of the m.o.'s is a crude one. Its chief advantage lies in its simplicity, and, as we shall show later in this chapter, it has been developed into a useful

technique for obtaining semiquantitative information about very elaborate molecules quickly. If we wish, we may dispense with the approximations (65), and use more elaborate orbitals containing several variable parameters. The values of such parameters, of course, may not be taken over from  $H_2^+$  without change; their values must be obtained by independent use of the variation method.

There are no less than four distinct levels which arise from the different ways of allotting two electrons to the m.o.'s  $\chi_g$  and  $\chi_u$  of (65). Two electrons can be put in  $\chi_g$  (as in 67) or two in  $\chi_u$  (as in 70), or one in each, with parallel or antiparallel spins (68, 69).

$${}^1\sum_g : \psi_I = \chi_g(1)\chi_g(2) [\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\sqrt{2} \quad (67)$$

$${}^3\sum_g : \psi_{II} = \frac{\alpha(1)\alpha(2)}{\beta(1)\beta(2)} [\chi_g(1)\chi_u(2) - \chi_u(1)\chi_g(2)] [\alpha(1)\beta(2) + \beta(1)\alpha(2)]/\sqrt{2} \quad (68)$$

$${}^1\sum_u \psi_{III} = [\chi_g(1)\chi_u(2) + \chi_u(1)\chi_g(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\sqrt{2} \quad (69)$$

$${}^1\sum_u : \psi_{IV} = \chi_u(1)\chi_u(2) [\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\sqrt{2} \quad (70)$$

In (67)–(70) the total wave function has to be antisymmetric, so that symmetric space parts, as in  $\psi_I, \psi_{III}, \psi_{IV}$ , must be associated with antisymmetric spin parts, and vice versa. Presumably  $\psi_I$  will correspond to the lowest energy among these four configurations, since it implies double occupancy of the bonding orbital  $\chi_g$ . In the same way  $\psi_{IV}$  should have the highest energy. If we accept (67) as an approximate molecular wave function the energy integral can be shown to give us

$$E = 2E_0 + \int \chi_g^*(1)\chi_g^*(2) \frac{1}{r_{12}} \chi_g(1)\chi_g(2) d\tau_1 d\tau_2 \quad (71)$$

where

$$E_0 = \int \chi_g^*(1)H_0(1)\chi_g(1) d\tau_1 \quad (72)$$

and  $H_0(1)$  is the one-electron Hamiltonian given in (51). Detailed numerical calculation gives for the dissociation energy the value 2.68 ev which may be compared with the corresponding Heitler-London value 3.14 ev.

The next stage in a complete calculation would be to introduce variable screening parameters, and polarization terms in the original atomic orbitals  $\phi_A, \phi_B$ . But instead of describing this, we shall consider another way of



improving the simple m.o. type of wave function. As we shall see, this new improvement has the result of identifying the new wave function with the covalent-ionic function of § 2.6.

### 2.8 Configuration Interaction

The four wave functions  $\psi_I$ — $\psi_{IV}$  of (67)—(70) are all of distinct symmetry except for the first and last, which both possess  $^1\Sigma_g$  symmetry. This implies that, since none of the four is an exact eigenfunction, we should be able to get improved approximations by mixing them. But the differing symmetries show that  $\psi_I$  and  $\psi_{IV}$  are the only ones that can mix in this way. Let us put

$$\psi_k = \psi_I(1,2) + k\psi_{IV}(1,2) \quad (73)$$

where  $k$  is a variable parameter. If we vary the energy integral subject to the condition that  $\psi_k$  is normalized we obtain the  $2 \times 2$  secular determinant for the stationary values of the energy  $E$ ,

$$\begin{vmatrix} H_{II} - E & H_{IIV} \\ H_{IVI} & H_{IVIV} - E \end{vmatrix} = 0. \quad (74)$$

The lower root corresponds to the ground state, and is lower than the energy  $H_{II}$  of the separate function  $\psi_I$ . The upper root will be some approximation (though probably not a very good one) to a very highly excited level of the molecule. But both such states must still have symmetry  $^1\Sigma_g$ .

The calculation of this energy leads to a dissociation energy  $D_0 = 4.00$  ev, at the equilibrium distance of 0.749 Å. These are just the values previously obtained in § 2.6 with covalent ionic resonance. This is no accident. The two functions are of identical form, as may be seen by writing them out in full. Thus, apart from a normalizing factor (73) may be written (omitting the constant spin term  $\alpha(1)\beta(2) - \beta(1)\alpha(2)$  and the normalization factors in  $\psi_{\text{cov}}$ ,  $\psi_{\text{ion}}$ )

$$\begin{aligned} \psi_k &= [\phi_A(1) + \phi_B(1)] [\phi_A(2) + \phi_B(2)] + k[\phi_A(1) - \phi_B(1)] [\phi_A(2) - \phi_B(2)] \\ &= (1 - k) [\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)] + (1 + k) [\phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2)] \\ &= (1 - k)\psi_{\text{cov}} + (1 + k)\psi_{\text{ion}} \\ &= \psi_{\text{cov}} + \lambda\psi_{\text{ion}}, \end{aligned} \quad (75)$$

where  $\lambda = (1 + k)/(1 - k)$ . Thus the method of molecular orbitals, allowing for this interaction of configurations, becomes identical with the method of Heitler and London, with allowance for ionic terms. This result, which we

have just shown rigorously for  $H_2$ , holds quite generally. In other words, the valence-bond (v.b.) method including ionic structures is ultimately equivalent to the molecular-orbital method with configuration interaction. (This latter procedure is sometimes labelled the LCAO MO CI method!) In large molecules, however, the number of configurations of given symmetry which can interact is exceedingly large: and so is the number of ionic and similar structures in the v.b. scheme. So we are usually compelled to restrict our choice. And then the two methods are no longer entirely equivalent. Fortunately, however, they are usually in close agreement with each other.

When there are more than two electrons in the molecule, we can no longer split off the spin and space parts of the total wave function. We then form our wave function out of spin-orbitals. A spin-orbital is a function involving both space and spin, but referring only to one electron, as for example  $\chi_g(1)\alpha(1)$  or  $\chi_g(1)\beta(1)$ . A closed-shell (singlet) system can then be represented by a single determinant, but situations in which each space orbital is not necessarily doubly-occupied will require a linear combination of determinants. For example,  $\psi_I$  in (67) may be written

$$^1 \sum_g : \psi_I = \begin{vmatrix} \chi_g(1)\alpha(1) & \chi_g(1)\beta(1) \\ \chi_g(2)\alpha(2) & \chi_g(2)\beta(2) \end{vmatrix} \quad (76)$$

and (69)

$$^1 \sum_u : \psi_{III} = \begin{vmatrix} \chi_g(1)\alpha(1) & \chi_u(1)\beta(1) \\ \chi_g(2)\alpha(2) & \chi_u(2)\beta(2) \end{vmatrix} - \begin{vmatrix} \chi_g(1)\beta(1) & \chi_u(1)\alpha(1) \\ \chi_g(2)\beta(2) & \chi_u(2)\alpha(2) \end{vmatrix}. \quad (77)$$

The methods for constructing spin eigenfunctions from determinants of spin-orbitals are precisely those used in the case of complex atoms. One advantage of the method of molecular orbitals is that it generalizes this atomic technique to apply to molecules.

## 2.9 The James-Coolidge Wave Function for $H_2$

All our accounts of  $H_2$  have so far been based on the use of atomic orbitals. But this is not necessary, and indeed presents considerable difficulty in the introduction of sufficient flexibility to get a really accurate energy. The most accurate function of this kind is due to James and Coolidge<sup>16</sup> who showed that the type of function represented in (42) could be adapted to this purpose. Let  $\lambda_1, \mu_1$ , and  $\lambda_2, \mu_2$  be the coordinates for the two electrons. And let  $r_{12}$  be the distance between them. Then a function constructed as a linear combination of terms such as

$$e^{-a(\lambda_1 + \lambda_2)} \lambda_1^m \lambda_2^n \mu_1^p \mu_2^q \left( \frac{r_{12}}{R} \right) \quad (78)$$

### 3. CHEMICAL BINDING

can be made to approach as closely as we like to the true eigenfunction provided that sufficient terms are included. James and Coolidge included no less than 15 such independent terms. (On account of symmetry certain terms must have the same numerical coefficient, so the total number of terms was almost twice as large.) This impressive calculation led to an energy value and internuclear distance inappreciably different from the observed ones. We shall not discuss this particular function further, because, despite its great success, it does not seem possible to assign any physical meaning to the individual terms such as (78) in the sum, and there seems effectively no way of generalizing the analysis to deal with more complicated molecules.

#### 2.10 Homonuclear Diatomic Molecules

The molecular-orbital description, generally without the introduction of configuration interaction, is much favoured by spectroscopists, who want not so much to calculate the energy of a transition with great exactitude, as to interpret a molecular excitation as due chiefly to the excitation of an electron from one molecular orbital to another. In this respect it is much more descriptive than the valence-bond method. We illustrate the use of the m.o. method in a qualitative sense, both for characterizing the ground state and for interpreting certain electronic transitions, by reference to some homonuclear diatomic molecules, e.g.,  $\text{Li}_2$ ,  $\text{N}_2$ ,  $\text{F}_2$ .

We may list the assumptions made in this treatment, as follows:

(1) A molecular state is represented with adequate accuracy by one configuration of spin-orbitals. This is equivalent to stating which of the possible allowed spin-orbitals are occupied, and includes a statement about the resultant spin.

(2) To each spin-orbital there is an energy eigenvalue, and these one-electron energies obey the noncrossing rule of § 1.10.

(3) For many purposes the LCAO representation is adopted for each molecular orbital. In such a situation only atomic orbitals (a.o.'s) of approximately equal energy will mix together effectively. Symmetry properties such as  $\sigma, \pi, \delta, \dots$  and  $g, u$  serve further to define the m.o.'s and limit the mixing of a.o.'s.

(4) Earlier in this chapter we labelled molecular orbitals exclusively by their symmetry properties. But we need, in addition, some indication of their energy, which should correspond, in molecular situations, to the principal quantum number in atoms, e.g.,  $1s, 2s, 3s, \dots$ . Without such indication we cannot distinguish m.o.'s of the same symmetry. This may

be done in several distinct ways. The first, historically, is by writing the state of the united atom to which the molecular state tends as  $R \rightarrow 0$ . (For example, the lowest two states  $\chi_g$  and  $\chi_u$  in (31) for the  $H_2^+$  ion are called  $1s\sigma_g$  and  $2p\sigma_u$  respectively.) This scheme is convenient for small molecules with few electrons, but becomes very cumbersome if the united atom is much heavier than either of the two constituent atoms. The second way of labelling the m.o.'s is by reference to the levels of the separated atoms into which the m.o. splits up when  $R \rightarrow \infty$ . We must also indicate whether the orbital is bonding or antibonding. (In this scheme the two lowest states of  $H_2^+$  would be  $\sigma 1s$  and  $\sigma^* 1s$ .) This scheme is not directly applicable to heteronuclear molecules because in general the LCAO MO will involve different atomic orbitals from the two atoms (see below). The third description is simply to specify the  $\sigma, \pi, \dots$  character and then to use the letters of the alphabet to label orbitals in order of ascending energy, so far as this may be deduced from spectroscopic evidence, with the little  $z$  being used for the lowest. Finally, by analogy with atomic levels, we may describe the orbitals as  $1\sigma, 2\sigma, 3\sigma, \dots; 1\pi, 2\pi, \dots$  in which the energy increases in each group in the sequence shown. It seems likely that ultimately some notation such as the last of this series will become universally acceptable. We could make the following comparison

separated atom designation	$\sigma 1s$	$\sigma^* 1s$	$\sigma 2s$	$\sigma^* 2s$	$\sigma 2p$	$\pi, 2p$	$\pi^*, 2p$	$\sigma^* 2p$
						$\pi, 2p$	$\pi^*, 2p$	
energy sequence notation			$z\sigma$	$y\sigma$	$x\sigma$	$w\pi$	$v\pi$	$u\sigma$
"atomic parallel" notation	$1\sigma$	$2\sigma$	$3\sigma$	$4\sigma$	$5\sigma$	$1\pi$	$2\pi$	$6\sigma$

( $\sigma$  orbitals are nondegenerate, but  $\pi, \delta, \dots$  orbitals are each doubly-degenerate, as in § 1.6). The relation between these notations and that for the united atom is illustrated in the correlation diagram in Fig. 8.

(5) The electrons are now fed in to the allowed levels as in the "aufbau" principle described in § 2.4.

It will often happen that both the bonding and antibonding m.o.'s are occupied. The result of this is equivalent to a small net repulsion. Such a conclusion follows from the argument that for a homonuclear molecule for which the one-electron Hamiltonian is  $H$ , the bonding orbital  $\phi_A + \phi_B$  has an energy

$$E_+ = \frac{E_A + \beta}{1 + S} = E_A + \frac{\beta - E_A S}{1 + S}$$

where

$$\beta = \int \phi_A^* H \phi_A d\tau$$

and

$$\beta = \int \phi_A^* H \phi_B d\tau = \int \phi_B^* H \phi_A d\tau.$$

Similarly the antibonding orbital  $\phi_A - \phi_B$  has an energy

$$E_- = \frac{E_A - \beta}{1 - S} = E_A - \frac{\beta - E_A S}{1 - S}$$

The overlap integral  $S$  will usually be such that  $0 < S < 1$ , so that  $0 < 1/(1 + S) < 1/(1 - S)$ . Hence the sum  $E_+ + E_-$  is greater than  $2E_A$ , provided (as actually occurs) that  $\beta - E_A S$  is negative.

### 2.11 Some Examples of m.o. Descriptions

We may illustrate the above principles by some particular examples

(1)  $H_2$ :  $(\sigma 1s)^2$ , i.e., two electrons in the lowest m.o. An excited state arises from the description  $(\sigma 1s)(\sigma^* 1s)$ .

(2)  $He_2^+$ :  $(\sigma 1s)^2(\sigma^* 1s)$ . The Pauli principle does not permit more than two electrons to be assigned to any one space orbital, e.g.,  $(\sigma 1s)$ . The third electron must therefore go into  $(\sigma^* 1s)$ .

(3)  $He_2$ :  $(\sigma 1s)^2(\sigma^* 1s)^2$ . We should expect this to be unstable, as indeed it is. But excited states such as  $(\sigma 1s)^2(\sigma^* 1s)(\sigma 2s)$  which would dissociate into one normal helium atom and one excited atom would be stable. More accurately these states would be metastable, since the transition to the unstable ground level is a forbidden one. Such metastable helium molecules are well-known experimentally.

(4)  $Li_2$ : each separate atom has one  $2s$  valence electron outside a closed  $K$  shell. So the ground state of the molecule would be  $KK(\sigma 2s)^2$ .

(5)  $N_2$ : the separate N atom has a configuration  $K(2s)^2(2p)^3$ . So the rules (2)–(4) lead to a molecular description

$$KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p)^2(\pi, 2p)^2(\pi, 2p)^2.$$

The abbreviated notation for this would be

$$KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4$$

or, alternatively,

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^4.$$

The  $(\sigma 2s)^2$  and  $(\sigma^* 2s)^2$  electrons roughly cancel one another so far as bonding is concerned, so that the binding comes largely from  $(\sigma 2p)^2(\pi, 2p)^2(\pi, 2p)^2$ .

(6)  $O_2$ : The atom is  $K(2s)^2(2p)^4$ . So the rules give

$$KK(x\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^2. \quad (79)$$

The pair of orbitals ( $x\sigma$ ) and ( $y\sigma$ ) will largely cancel, and so will two of the ( $w\pi$ )<sup>4</sup> orbitals with the two ( $v\pi$ ) orbitals. The main contribution to the bonding is therefore due to ( $x\sigma$ )<sup>2</sup> ( $w\pi$ )<sup>2</sup>. All the examples (1)–(5) have been singlets since each orbital is doubly occupied, with the single exception of  $\text{He}_2^+$  which is a doublet. But there remains some doubt about the configuration given in (79) for  $\text{O}_2$ . This is because there are two electrons to be put in one or both of the ( $v\pi$ ) orbitals ( $\pi_y 2p$ ) and ( $\pi_x 2p$ ). Proceeding as for atoms (Chapter 1, § 11, in this volume) we find that the two electrons prefer to go into separate orbitals, and have parallel spin. One advantage of the m.o. method is that we may “carry over” many of the rules for atoms without any great alteration. In this case we predict that the ground state will be a triplet, with description (in separated atom language)

$$KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p)^2 (\pi_y 2p)^2 (\pi_x 2p)^2 (\pi_y^* 2p) (\pi_x^* 2p).$$

It was one of the early triumphs of m.o. theory that Lennard-Jones<sup>17</sup> was able to explain the experimental paramagnetism of  $\text{O}_2$  in this way.

## 2.12 Heteronuclear Diatomics

Very similar situations arise with heteronuclear molecules. In the m.o. account we still use the LCAO approximation, taking a  $\phi_A$  from one atom and a  $\phi_B$  from the other. But in general these will not be similar orbitals. They must, of course, have the same  $\sigma, \pi, \dots$  character, and they must have approximately equal energy. For otherwise the extent of their mixing is negligibly small. Two examples will show how this works out.

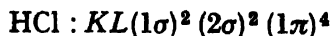
(7)  $\text{HCl}$ : the hydrogen atom has just one electron in a  $1s$  orbital. The chlorine atom has two completely filled shells  $K, L$  and then seven electrons in the valence shell, with a description  $KL(3s)^2 (3p)^5$ . The  $K$ - and  $L$ -shell electrons are far too low in energy to mix with the hydrogen  $1s$ , and the  $3p_y$  and  $3p_z$  orbitals are of the wrong symmetry ( $\pi$  type) if the  $x$ -axis lies along the line of nuclei. There may be a little mixing of the  $3s$  electron orbitals with the hydrogen, but, on energy grounds, this will be small.

The bonding orbital is built up largely from  $3p_x$  of chlorine and  $1s$  of hydrogen in an orbital of form  $c_1\text{Cl}(3p_x) + c_2\text{H}(1s)$ . The numerical coefficients  $c_1$  and  $c_2$  must be chosen by some variational process, and their difference is an indication of the polarity of the molecule. It will turn out that  $c_1 > c_2$ , so that more of the bonding charge cloud is around the chlorine nucleus than the hydrogen. This is sometimes expressed by saying that

+→

there is a dipole moment  $\text{H} \text{Cl}$ , with polarity  $\text{H}^+\text{Cl}^-$ . Its magnitude, which

is directly related to the ratio  $c_1 : c_2$  is  $1.03 \times 10^{-18}$  esu. (i.e., 1.03 Debyes). So we could write the electron description as



where  $(1\sigma)$  is closely  $\text{Cl}(3s)$  and  $(2\sigma)$  is the bonding orbital. One of the great advantages of the m.o. method is the fundamentally easy way in which it handles the polarity of a bond.

(8) NO: here the description is  $KK(z\sigma)^2 (y\sigma)^2 (x\sigma)^2 (w\pi)^4 (v\pi)$ , where  $(z\sigma)$  is mostly  $\text{O}(2s)$ ;  $(y\sigma)$  is mostly  $\text{N}(2s)$ ;  $(x\sigma)$  is a combination of  $\text{O}(2p_x)$  and  $\text{N}(2p_x)$ ;  $(w\pi)$  is a combination of  $\text{O}(2p_y)$  and  $\text{N}(2p_y)$ , or  $\text{O}(2p_z)$  and  $\text{N}(2p_z)$ , and  $(v\pi)$  is a different combination of  $\text{O}(2p_y)$  and  $\text{N}(2p_y)$ . Thus the ground state is a doublet, with one unpaired electron.

It is possible to represent this in valence-bond language. Thus in HCl, we say that all the electrons are in undisturbed atomic orbitals except the  $\text{H}(1s)$  and  $\text{Cl}(3p_x)$  electrons, which are now paired together in the manner of Heitler and London. But to allow for the polar character of the molecule we must expect a larger contribution from the ionic function representing  $\text{H}^+\text{Cl}^-$  in the covalent-ionic wave function analogous to (64), than in the case of  $\text{H}_2$ :

$$\psi(\text{H} - \text{Cl}) = \psi_{\text{cov}} + \lambda\psi_{\text{ion}}. \quad (80)$$

We refer to this function by saying that it allows for covalent-ionic resonance. This technique has been extensively exploited in an ingenious manner by Pauling and others to provide semiquantitative explanations of various molecular phenomena. We shall not pursue the matter here because it is not so easily adapted to quantitative calculation, and — as the reader will soon see if he tries to provide an account of either  $\text{O}_2$  or NO — it leads to no simple physical picture of the bonding. Further details of the method may be found either in Pauling's own book "The Nature of the Chemical Bond,"<sup>18</sup> in Wheland's "Theory of Resonance,"<sup>19</sup> or in Coulson's "Valence."<sup>20</sup>

### 2.13 Multiple Bonds

In the examples (1)–(8) above,  $\text{H}_2$ ,  $\text{Li}_2$  and HCl had one pair of electrons forming the bond between them,  $\text{O}_2$  had two pairs and  $\text{N}_2$  had three pairs mainly responsible for the bonding. Now for the last 100 years chemists have held the notion of single, double and triple bonds, distinguished by characteristic lengths, and reactions.  $\text{H}_2$  and  $\text{Li}_2$  would be assigned single bonds,  $\text{O}_2$  a double bond and  $\text{N}_2$  a triple bond, written  $\text{H} - \text{H}$ ,  $\text{Li} - \text{Li}$ ,  $\text{O} = \text{O}$ ,  $\text{N} \equiv \text{N}$ . It is interesting to see how this is reflected in the m.o. account which we have given. In general, we may say that

a single bond has a description  $\sigma^2$

a double bond has a description  $\sigma^2\pi^2$

a triple bond has a description  $\sigma^2\pi^4$ .

According to this description, the odd-electron molecule NO with five effective bonding electrons would be halfway between a double and a triple bond. We could even say that its bond order was  $2\frac{1}{2}$ !

## 2.14 Polyatomic Molecules: Water $\text{H}_2\text{O}$

The simple LCAO MO method is readily extended to polyatomic molecules, though we shall find it desirable to make some further simplifying assumptions suggested by chemical knowledge. The chief difference between polyatomic and diatomic molecules will lie in the fact that each molecular orbital will be polycentric instead of bicentric.

Consider first the water molecule  $\text{H}_2\text{O}$ . X-ray and spectroscopic evidence shows that the molecule is in the form of an isosceles triangle with the HOH angle equal to  $104^\circ 31'$ . Since the  $\text{H}_1 \dots \text{H}_2$  distance is about 1.6 Å, considerably greater than normal H...H distances in molecular hydrogen (0.7 Å) this implies that the chief binding is between the oxygen atom and each separate hydrogen. Bearing in mind the description of the oxygen atom in (6) of § 2.11 we shall anticipate that the orbitals available for the formation of these bonds are two  $2p$  orbitals. If we take the  $x$ - and  $y$ -axes as shown in figure 13, with the  $z$ -axis normal to the plane of the molecule, we may call these the  $2p_x$  and  $2p_y$  atomic orbitals. Let us denote their wave

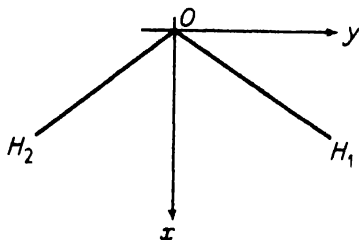


FIG. 13.  $\text{H}_2\text{O}$  notation.

functions by  $\phi_O(x)$  and  $\phi_O(y)$ , and the two hydrogen orbitals by  $\phi_{H_1}$  and  $\phi_{H_2}$ . Then since the molecule is invariant under reflection in the  $xz$  plane we shall have to separate our m.o.'s into those which are symmetrical and those which are antisymmetrical with respect to this plane. This leads to possible LCAO forms

$$\begin{aligned}\psi_+ &= \phi_O(x) + \lambda_+(\phi_{H_1} + \phi_{H_2}) \\ \psi_- &= \phi_O(y) + \lambda_-(\phi_{H_1} - \phi_{H_2}).\end{aligned}\tag{81}$$



### 3. CHEMICAL BINDING

We next suppose that there is an effective Hamiltonian  $H$  for each electron.<sup>†</sup> Then we may minimize the energy integral  $\int \psi^* H \psi d\tau / \int \psi^* \psi d\tau$ . This leads to secular equations for the energies of  $\psi_+$  and  $\psi_-$ , and from which the variable parameters  $\lambda_+$  and  $\lambda_-$  may be obtained. For the  $\psi_+$  functions

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - E \end{vmatrix} = 0 \quad (82)$$

and for the  $\psi_-$  functions

$$\begin{vmatrix} H_{33} - E & H_{34} - ES_{34} \\ H_{43} - ES_{43} & H_{44} - E \end{vmatrix} = 0 \quad (83)$$

where

$$H_{ij} = \int \chi_i^* H \chi_j d\tau, \quad S_{ij} = \int \chi_i^* \chi_j d\tau$$

and

$$\begin{aligned} \chi_1 &= \phi_O(x), & \chi_2 &= N_2(\phi_{H_1} + \phi_{H_2}) \\ \chi_3 &= \phi_O(y), & \chi_4 &= N_4(\phi_{H_1} - \phi_{H_2}). \end{aligned}$$

$N_2$  and  $N_4$  are normalizing factors which, because of the large  $H_1 \dots H_2$  distance, are both nearly equal to  $1/\sqrt{2}$ . It will be noticed that on account of their differing symmetry there is no mixing between the two groups of orbitals. This is because all integrals such as  $H_{13}$  and  $S_{13}$  vanish identically. In this way we simplify the full secular determinant which, without our device of choosing symmetrical and antisymmetrical combinations of  $\phi_{H_1}$  and  $\phi_{H_2}$ , would have been of order  $4 \times 4$ .

Let us now make the simplifying assumption that the overlap integrals  $S_{ij}$  are all zero. This will simplify our analysis without significantly affecting the result. Then (82) and (83) lead to

$$\begin{aligned} E_+ &= \frac{1}{2}(H_{11} + H_{22}) \pm \frac{1}{2}[(H_{11} - H_{22})^2 + 4|H_{12}|^2]^{1/2} \\ E_- &= \frac{1}{2}(H_{33} + H_{44}) \pm \frac{1}{2}[(H_{33} - H_{44})^2 + 4|H_{34}|^2]^{1/2}. \end{aligned} \quad (84)$$

There are four energy values. This is to be expected since, if we start with four atomic orbitals  $\phi_O(x)$ ,  $\phi_O(y)$ ,  $\phi_{H_1}$  and  $\phi_{H_2}$ , it must be possible to form four molecular orbitals out of them. If we take the negative signs in (84) we get bonding orbitals. Let us put two electrons in each. This should provide us with an estimate of the energy of the ground state. If we put  $H_{11} = H_{33}$ ,  $H_{22} = H_{44}$ , and neglect  $\int \phi_{H_1}^* H \phi_{H_2} d\tau$ , then

$$E_{\text{tot}} = 2(H_{11} + H_{22}) - [(H_{11} - H_{22})^2 + 4|H_{12}|^2]^{1/2} - [(H_{11} - H_{22})^2 + 4|H_{34}|^2]^{1/2}.$$

<sup>†</sup> This matter is discussed more generally in § 2.17.

This energy depends on the valence angle  $2\alpha$ . The value of this angle occurs implicitly only in  $H_{12}$  and  $H_{34}$ . If we may suppose that  $\phi_O(x)$  is resolved into the sum of two oxygen  $2p$  orbitals, respectively along ( $\phi_{||}$ ) and perpendicular ( $\phi_{\perp}$ ) to the line  $O - H_1$  then

$$\begin{aligned} H_{12} &= N_2 \int \phi_O(x) H(\phi_{H_1} + \phi_{H_2}) d\tau = 2N_2 \int \phi_O(x) H \phi_{H_1} d\tau \\ &= 2N_2 \int (\phi_{||} \cos \alpha + \phi_{\perp} \sin \alpha) H \phi_{H_1} d\tau. \end{aligned}$$

Now in the neighbourhood of the bond  $O - H_1$ , where alone the product  $\phi_O \phi_{H_1}$  is reasonably large, the effective Hamiltonian  $H$  will possess almost an axial symmetry around  $OH_1$ . Then, on account of the difference in symmetry between  $\phi_{\perp}$  and  $\phi_{H_1}$  the term in  $\sin \alpha$  will vanish. So

$$H_{12} \approx 2N_2 \cos \alpha \beta_{OH} \quad \text{where} \quad \beta_{OH} = \int \phi_{||} H \phi_{H_1} d\tau.$$

Similarly

$$H_{34} \approx 2N_4 \sin \alpha \beta_{OH}.$$

Hence

$$\begin{aligned} E_{\text{tot}} \approx 2(H_{11} + H_{22}) - [(H_{11} - H_{22})^2 + 16N_2^2 \cos^2 \alpha \beta_{OH}^2]^{1/2} - \\ [(H_{11} - H_{22})^2 + 16N_4^2 \sin^2 \alpha \beta_{OH}^2]^{1/2}. \end{aligned}$$

We have already seen that  $N_2^2 \approx N_4^2 \approx \frac{1}{2}$ . Then simple differentiation with respect to  $\alpha$  shows that  $E_{\text{tot}}$  has its minimum value when  $\tan \alpha = 1$ , irrespective of the values of  $H_{11}$ ,  $H_{22}$  and  $\beta_{OH}$ . Presumably if we had taken into account some of the small neglected terms we should have concluded that the equilibrium valence angle  $HOH$  should be approximately  $90^\circ$ . The observed value is in this region, but a little larger,  $104^\circ 31'$ . In this way valence angles may be predicted.

If we accept our approximations, then, at the minimum  $\lambda_+ = \lambda_-$  in (81). This has an interesting consequence. For the wave function  $\Psi$  corresponding to double occupancy of the stable orbitals  $\psi_+$  and  $\psi_-$  is

$$\begin{aligned} \Psi = \begin{vmatrix} \psi_+(1)\alpha(1) & \psi_+(1)\beta(1) & \psi_-(1)\alpha(1) & \psi_-(1)\beta(1) \\ \psi_+(2)\alpha(2) & \psi_+(2)\beta(2) & . & . \\ . & . & \psi_-(3)\alpha(3) & . \\ . & . & . & \psi_-(4)\beta(4) \end{vmatrix} \end{aligned} \quad (85)$$

Now let us add and subtract the first and third columns, and also the second

and fourth columns, to give the entirely equivalent determinant (apart from normalization)

$$\Psi = \begin{vmatrix} \psi_I(1)\alpha(1) & \psi_I(1)\beta(1) & \psi_{II}(1)\alpha(1) & \psi_{II}(1)\beta(1) \\ \psi_I(2)\alpha(2) & \psi_I(2)\beta(2) & & \\ & & \psi_{II}(3)\alpha(3) & \\ & & & \psi_{II}(4)\beta(4) \end{vmatrix} \quad (86)$$

where

$$\begin{aligned} \psi_I &= \psi_+ + \psi_- = \phi_O(x) + \phi_O(y) + (\lambda_+ + \lambda_-)\phi_{H_1} + (\lambda_+ - \lambda_-)\phi_{H_2} \\ \psi_{II} &= \psi_+ - \psi_- = \phi_O(x) - \phi_O(y) + (\lambda_+ - \lambda_-)\phi_{H_1} + (\lambda_+ + \lambda_-)\phi_{H_2} \end{aligned}$$

Putting  $\lambda_+ = \lambda_- = \lambda$  and  $\alpha = 45^\circ$ , this gives

$$\begin{aligned} \psi_I &= \sqrt{2} \phi_{O_1} + 2\lambda \phi_{H_1} \\ \psi_{II} &= \sqrt{2} \phi_{O_2} + 2\lambda \phi_{H_2} \end{aligned}$$

where  $\phi_{O_1}$  and  $\phi_{O_2}$  are  $2p$  atomic orbitals of the oxygen atom with their axes directed along the lines  $O - H_1$  and  $O - H_2$  respectively. We call  $\psi_I$  and  $\psi_{II}$  localized orbitals, since they are localized with their concentration of charge in the region of the two "chemical" bonds. It is important to realize that in this case the description (85) in terms of delocalized orbitals is neither better nor worse than the description (86) in terms of localized orbitals. If we are interested in excited electronic levels, then (85) is usually the more satisfactory type of wave function, for the simple reason that  $\psi_+$  and  $\psi_-$  are already related to the symmetry properties of the whole molecule, whereas  $\psi_I$  and  $\psi_{II}$  are not. But (86) is more related to the ideas implied in the term chemical bond. This is because, if we were to replace the second hydrogen atom  $H_2$  by some other atom, or group of atoms, it is reasonable to suppose that only  $\psi_{II}$  would be significantly altered,  $\psi_I$  being concentrated in regions of space not affected by the replacement. Thus  $\psi_I$  may be said to determine the characteristic properties of the bond  $O - H_1$ , and these properties — length, dipole moment, energy, force constant, polarizability — should be largely independent of the nature of the other bonds in the molecule, and should be practically constant from molecule to molecule. The possibility of this localization is the fundamental reason for the existence of such characteristic bond properties. Historically the localized orbitals were used first, with the assumption that the bond  $O - H_1$  would be described by a molecular orbital composed of the hydrogen orbital  $\phi_{H_1}$  and a suitable oxygen orbital  $\phi_{O_1}$  directed so as to overlap with  $\phi_{H_1}$  as much as possible. It was only later that the equivalence of localized and delocalized descriptions was properly realized.

If we wished to carry this discussion further we should need to take account of the Coulomb and exchange forces exerted by the other electrons, hitherto neglected; and we should need to make a much more detailed study of  $\beta_{\text{OH}}$  and the proper one-electron Hamiltonian to use. A brief account of some of this work is described in § 2.18. In the form in which we have described this work, it is usually called semiempirical, since considerable assumptions are made, and the values of some of the fundamental parameters such as  $\beta_{\text{OH}}$  are often obtained by reference to some type of experimental evidence, such as bond length or energy.

A similar discussion to (86) could be in terms of localized bonds, using the valence-bond scheme. But now each separate O-H bond is described as a covalent pairing of two orbitals as, e.g.,  $\phi_{\text{O}}$  and  $\phi_{\text{H}}$ , and then the complete wave function is made antisymmetrical. But on this scheme there is no analogue to the delocalized description (85). Furthermore the results of the simple treatment are very similar to those of the simple m.o. treatment, but the corresponding more elaborate treatment is almost unmanageable. We shall not therefore discuss this matter further.

### 2.15 Hybridization: The Carbon Atom

In our account of  $\text{H}_2\text{O}$  it was not difficult to write down the form of the appropriate LCAO MO's. This is not always the case. As a very important example consider the carbon atom. Its lowest atomic configuration is  $(1s)^2 (2s)^2 (2p_x) (2p_y)$  with two unpaired electrons, suggesting a divalent character similar to that of oxygen discussed in the preceding section. But we know that carbon is far more often tetravalent than divalent. This situation is best understood by introducing a new concept — hybridization.

In the first place there are well-known atomic states of carbon with the configuration  $(1s)^2 (2s) (2p_x) (2p_y) (2p_z)$  in which one of the 2s electrons has been excited to the remaining 2p orbital. The excitation energy of the lowest such transition is only 96 kcal mole<sup>-1</sup> (i.e., just over 4 ev). But the atom in this excited state has four unpaired electrons, and so could be expected to be able to form four bonds. If the energy of the two new bonds was greater than the energy of excitation, it would be profitable to make the excitation, and subsequently recover in the two additional bonds more energy than had been expended on the excitation. This is precisely what happens. But the matter cannot be dealt with quite so simply. For if we followed our experience with  $\text{H}_2\text{O}$  and formed four localized bonds with the atomic 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub> orbitals, they would not all be equivalent: there would be three of one kind, very similar to the O-H bonds in water, and a fourth involving

the single  $2s$  orbital. This situation is not found experimentally, for all four C-H bonds in the simplest of such compounds — methane  $\text{CH}_4$  — are known to be equivalent, and their mutual angle is the familiar tetrahedral angle  $109^\circ 28'$ . The only way to avoid this inequivalence is to suppose that instead of making localized bonds with the separate  $2s$  and  $2p$  orbitals, we make localized bonds using a mixture of them. Such linear combinations, or hybrids, were first introduced by Pauling,<sup>21</sup> who showed that the combinations

$$\begin{aligned} t_a &\equiv \frac{1}{2}[\phi(s) + \phi(2p_x) + \phi(2p_y) + \phi(2p_z)] \\ t_b &\equiv \frac{1}{2}[\phi(s) + \phi(2p_x) - \phi(2p_y) - \phi(2p_z)] \\ t_c &\equiv \frac{1}{2}[\phi(s) - \phi(2p_x) + \phi(2p_y) - \phi(2p_z)] \\ t_d &\equiv \frac{1}{2}[\phi(s) - \phi(2p_x) - \phi(2p_y) + \phi(2p_z)] \end{aligned} \quad (87)$$

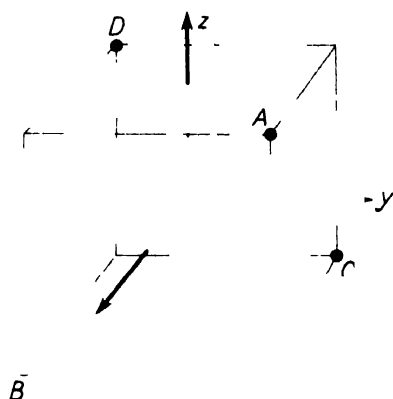


FIG. 14.  $\text{CH}_4$  O is the position of the carbon nucleus, A, B, C, D, those of the hydrogen nuclei.

were all linearly independent, and at the same time equivalent. Their only difference is that they are directed with axes of symmetry in different directions. With the notation of Fig. 14 we may write

$$t_a = \frac{1}{2}[\phi(s) + \sqrt{3}\phi(2p_a)] \quad (88)$$

where  $\phi(2p_a)$  is an atomic orbital in the  $(1,1,1)$  direction OA. Similarly

$$t_b = \frac{1}{2}[\phi(s) + \sqrt{3}\phi(2p_b)]$$

where  $\phi(2p_b)$  is an atomic orbital in the  $(1,-1,-1)$  direction OB. Similar results hold for  $t_c$  and  $t_d$ . Thus  $t_a$  has axial symmetry around the direction OA, and on account of the ungerade character of all  $p$  functions,  $t_a$  has its

maximum value on the line OA. Now if we place our four hydrogen atoms at positions such as A,B,C,D, we can form localized bonds by linear combinations of  $t_a$  and  $\phi(H_a)$ ,  $t_b$  and  $\phi(H_b)$ , etc. These bonds are all equivalent, and they are correctly oriented at the tetrahedral angle. Each such localized molecular orbital will be of the form  $t_a + \lambda\phi(H_a)$  with the same parameter  $\lambda$ , to be determined from a variational calculation.

There is an alternative way by which the particular combinations (87) could have been found. We say first that as a result of the four H atoms at positions A, ..., D the local field around the carbon atom at O is of tetrahedral symmetry. We then ask what linear combinations of spherical harmonics of order 2 (the  $p$  orbitals) has this symmetry. This leads us at once to the combinations of  $\phi(2p_x)$ ,  $\phi(2p_y)$  and  $\phi(2p_z)$  which appear in (87). The general problem of constructing hybrids has been solved in an elegant manner by Altmann (Chapter 2, § 6.5)

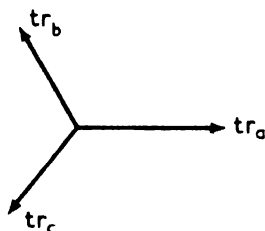


FIG. 15. Trigonal hybrids.

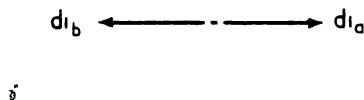


FIG. 16. Digonal hybrids

In (87) we used equal proportions of one  $s$  orbital and three  $p$  orbitals. We therefore speak of  $sp^3$  hybrids — though, as (88) suggests, each particular hybrid could be thought of as if it were  $s^{1/4}p^{3/4}$ . But we could equally well have considered hybrids arising from  $sp^2$ . There will be three of these, each  $s^{1/3}p^{2/3}$ . They take the form

$$\begin{aligned} tr_a &= \sqrt{\frac{1}{3}} [\phi(s) + \sqrt{2} \phi(2p_x)] \\ tr_b &= \sqrt{\frac{1}{3}} [\phi(s) + \sqrt{\frac{2}{3}} \phi(2p_y) - \sqrt{\frac{2}{3}} \phi(2p_x)] \\ tr_c &= \sqrt{\frac{1}{3}} [\phi(s) - \sqrt{\frac{2}{3}} \phi(2p_y) - \sqrt{\frac{2}{3}} \phi(2p_x)] \end{aligned} \quad (89)$$

and lead to three trigonal hybrids directed as in Fig. 15, in which the central atom is supposed to be at the origin, and the directions of the hybrids are shown by the three arrows. By analogy with (88) we could write these

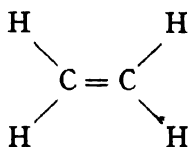
$$tr_a = \sqrt{\frac{1}{3}} [\phi(s) + \sqrt{2} \phi(2p_a)], \quad tr_b = \sqrt{\frac{1}{3}} [\phi(s) + \sqrt{2} \phi(2p_b)], \quad \text{etc.} \quad (90)$$

In the same way there are digonal hybrids  $sp$  formed by one  $s$  and one  $p$  orbital. Their form is

$$d_{1a} = \sqrt{\frac{1}{2}} [\phi(s) + \phi(2p_x)], \quad d_{1b} = \sqrt{\frac{1}{2}} [\phi(s) - \phi(2p_x)], \quad (91)$$

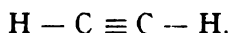
with directions as in Fig. 16.

An example of the need for trigonal hybrids is in ethylene ( $C_2H_4$ )



This is a planar molecule with all the valence angles close to  $120^\circ$ . If each carbon atom is hybridized in the  $sp^2$  trigonal fashion, we may form localized  $\sigma$ -type bonds for the four C-H and the C-C bonds. This still leaves unused the  $2p_z$  atomic orbitals on each carbon atom (the  $z$  direction being perpendicular to the molecular plane). These two orbitals are now used to form a  $\pi$ -bond, as in § 2.13. In this way the bond between the two carbon atoms is a double bond  $C=C$  and we see why the valence angles are approximately  $120^\circ$ .

In a similar way the digonal hybrids are needed for acetylene ( $C_2H_2$ )



This is a linear molecule, as would follow from Fig. 16, with one  $\sigma$ - and two  $\pi$ -bonds linking the two carbon atoms. This justifies us in writing it as a triple bond  $C \equiv C$ .

## 2.16 Benzene and Other Aromatic Molecules

There is still one other type of molecule to be described. This is interesting because it presents a situation where we cannot localize all the valence electrons in bicentric orbitals to form  $\sigma$  or  $\pi$  bonds, but some of them must be assigned to delocalized orbitals. Such molecules, of which benzene ( $C_6H_6$ ) is the simplest example, occupy a role intermediate between the conventional simple molecules with localized bonds and metals where the valence electrons move over the complete crystal.

In the case of benzene, spectroscopic and X-ray evidence shows without any qualification that the molecule is planar, with the regular hexagonal

shape of Fig. 17. The hydrogen atoms lie symmetrically away from the six carbon atoms a, b, . . . , f.

Now first of all, the close similarity between this molecule and ethylene, where again all the angles are  $120^\circ$ , strongly suggests that we hybridize the carbon atoms in the  $sp^2$  trigonal manner, and then form localized  $\sigma$ -type orbitals for each C-C and each C-H bond. We may say that this provides us with an excellent and rigid molecular framework. But a simple counting

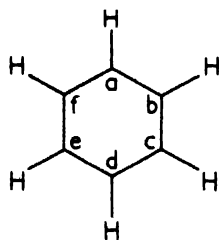
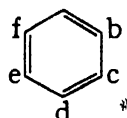
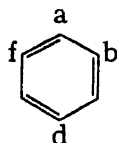


FIG. 17.  
 $C_6H_6$ : notation.

of electrons reveals that there remain six to be allotted to some sort of m.o.'s. They are the analogues of the  $2p_z$  electrons in ethylene. Let us call the six atomic orbitals in question  $\pi_a, \pi_b, \dots, \pi_f$ . We might have tried to form localized bicentric orbitals out of these  $\pi$  orbitals in a manner similar to that of ethylene, by choosing combinations  $\pi_a + \pi_b, \pi_c + \pi_d, \pi_e + \pi_f$ . This would have led to double bonds  $a = b, c = d, e = f$ , with a chemical bond diagram



But there is no particular reason why we should not have chosen other combinations  $\pi_b + \pi_c, \pi_d + \pi_e, \pi_f + \pi_a$ , leading to an alternative bond diagram



These two diagrams are often called Kekulé diagrams, after the chemist who imagined, 100 years ago, that the molecule was in some kind of dynamic oscillation from one to the other and then back again. Wave-mechanically we could represent this by a linear combination of the two wave functions which correspond to these diagrams; and we could speak of resonance between them. Such language is often used. But it is more instructive to abandon any attempt to find any localized description of these electrons, and instead, to form delocalized orbitals by linear combination of all six atomic orbitals. Thus we should try LCAO functions of the type

$$c_1\pi_a + c_2\pi_b + c_3\pi_c + \dots + c_6\pi_f, \quad (92)$$



with coefficients  $c_1, \dots, c_6$  to be determined. Fortunately, the great symmetry of this molecule ( $D_{6h}$ ) with its sixfold symmetry axis at right angles to the plane of the ring, enables us to write down their values without any trouble. A very convenient form (though not yet normalized) is

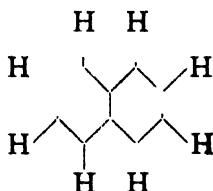
$$\pi_a + \omega \pi_b + \omega^2 \pi_c + \dots + \omega^5 \pi_f \quad (93)$$

where  $\omega$  is any quantity such that  $\omega^6 = 1$ . The relation of this to the cyclic rotation group (Chapter 2, § 6.1) will be immediately obvious. So also is its relation to the Bloch theorem in metals (Chapter 6, § 2.2), for the allowed values of  $\omega$  in (93) are simply the sixth roots of unity, viz.,

$$\omega = e^{2\pi i r/6} \quad r = 0, 1, 2, \dots, 5. \quad (94)$$

The m.o.'s corresponding to  $r = 0$  and  $r = 3$  are nondegenerate: those with  $r = 1$  and 5 are degenerate, being merely complex conjugates of each other: and so are  $r = 2$  and 4. In group theory terms, the orbital with  $r = 0$  is of symmetry  $a_{1g}$ , and with  $r = 3$ ,  $b_{2g}$ ;  $r = 1$  and 5 are  $e_{1g}$ , and  $r = 2$  and 4 are  $e_{2g}$ . If we wished we could pick out the real and imaginary parts of the degenerate m.o.'s and so obtain a purely real set of six orbitals. But this would disguise the quasi-metallic character of these delocalized orbitals. It turns out that the energies corresponding to  $r = 0, 1$ , and 5 are the lowest, so that these orbitals are just filled with the six available  $\pi$  electrons. The ground state is of symmetry  $A_{1g}$ , but when an electron is excited from one of the occupied to an unoccupied m.o. a considerable variety of possible symmetries arise.

More complicated molecules such as naphthalene  $C_{10}H_8$  can be built up in the same way. They are known chemically as aromatic hydrocarbons,



and their study forms one of the most fascinating chapters in organic chemistry. But their properties are entirely due to the two features which have already been described: (1) the formation of trigonal  $sp^2$  hybrids around each carbon atom, so leading to  $120^\circ$  valence angles and a planar molecular framework; and (2) delocalized  $\pi$  molecular orbitals for the electrons not already involved in the localized  $\sigma$ -type bonds. These  $\pi$  electrons behave rather like tiny electric currents in the rings, and are able to carry

electrical influences very easily from any one part of such a molecule to any other. For further details of all this the reader is referred to Coulson's "Valence"<sup>20</sup> or to "Quantum Chemistry" by Eyring, Walter and Kimball.<sup>23</sup>

## 2.17 Self-Consistent-Field Methods: The Equation for the Energy

We must now return to a rather more careful discussion of an approximation that we have already used on several occasions. For example, in § 2.14, when discussing the molecular orbitals for the water molecule we assumed that there was an effective one-electron Hamiltonian. This enabled us to deal with the valence electrons one at a time. Now the full Hamiltonian includes terms such as  $1/r_{12}$  which involve the simultaneous positions of two electrons. It is important to consider under what circumstances the full Hamiltonian can be replaced by a simpler effective Hamiltonian with only one-electron terms in it. We can approach this problem by a modification of the self-consistent-field theory of Hartree and Fock (Chapter 1, § 13.3).

Let us fix attention on the ground state of a molecule, in which we suppose that the molecular orbitals  $\phi_i$  ( $i = 1, 2, \dots, n$ ) are each doubly-occupied, and all other m o 's are entirely empty. We may take the  $\phi_i$  to be orthonormal, so that

$$\begin{aligned}\int \phi_i^* \phi_j d\tau &= 0 \quad i \neq j \\ &= 1 \quad i = j\end{aligned}\quad (95)$$

Our first step is to partition the complete Hamiltonian represented by (1), (2), and (5) into terms involving either only one, or two, electrons. In the simple case of the hydrogen molecule this is just what we did in (50) and (51). Thus we write

$$H = \sum_{2n} H^0(s) + \sum_{s < t} \frac{1}{r_{st}} \quad (96)$$

where the detailed form of  $H^0$  is

$$H^0(s) = -\frac{1}{2} \nabla_s^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{s\alpha}} \quad (97)$$

In (96) the first summation runs over all  $2n$  electrons, and the second summation is over all pairs of electrons  $s, t$ . In (97) the summation is over all nuclei  $\alpha$ .  $H^0(s)$  is sometimes called the core-Hamiltonian for electrons, since it is the sum of the kinetic energy and potential energy of attraction to all the nuclei, with complete omission of any interaction with any other electron.

The complete wave function is

$$\Psi(1,2,\dots,2n) = \sqrt{\left(\frac{1}{2n!}\right)} \text{Det} [\phi_1(1)\alpha(1), \phi_1(2)\beta(2), \phi_2(3)\alpha(3), \dots, \phi_n(2n)\beta(2n)] \quad (98)$$

where only the leading diagonal term in the determinant has been written down. On account of the orthonormality of the  $\phi_i$  this wave function is already normalized. The energy  $E$  associated with it is given, as usual, by

$$E = \int \Psi^* H \Psi d\tau_1 \dots d\tau_{2n}.$$

If we write (98) in the equivalent form

$$\Psi(1,2,\dots,2n) = \sqrt{\left(\frac{1}{2n!}\right)} \sum_P (-1)^P P \phi_1(1)\alpha(1) \phi_1(2)\beta(2) \dots \phi_n(2n)\beta(2n)$$

where the summation is over all  $(2n)!$  permutations  $P$  among the electrons, and  $(-1)^P$  means  $+1$  for even permutations, and  $-1$  for odd ones, then

$$E = \frac{1}{2n!} \int \sum_Q (-1)^Q Q \phi_1^*(1)\alpha^*(1) \dots \phi_n^*(2n)\beta^*(2n) \cdot H \cdot \sum_P (-1)^P P \phi_1(1)\alpha(1) \dots \phi_n(2n)\beta(2n) d\tau^{2n}.$$

Now every term in the first summation is a certain permutation of the leading diagonal term, and by a suitable change of labels of the electrons can be made to coincide with it. Such a change does not affect  $H$  which is completely symmetrical in the electrons; and its only effect on the second summation is to introduce a factor  $\pm 1$ , depending on whether the permutation  $Q$  is odd or even. The net result of all this is that every one of the  $(2n)!$  terms in the summation over permutations  $Q$  yields exactly the same integral. Hence we may drop the  $Q$  summation, and write

$$E = \int \phi_1^*(1)\alpha^*(1) \dots \phi_n^*(2n)\beta^*(2n) H \cdot \sum_P (-1)^P \phi_1(1)\alpha(1) \dots \phi_n(2n)\beta(2n) d\tau^{2n}. \quad (99)$$

When we insert in (99) the expression (96) for  $H$ , we have two sets of terms. The first member of the first set is

$$\int \phi_1^*(1)\alpha^*(1) \dots \phi_n^*(2n)\beta^*(2n) H^0(1) \sum_P (-1)^P \phi_1(1)\alpha(1) \dots \phi_n(2n)\beta(2n) d\tau^{2n}.$$

On account of the orthogonality of the  $\phi$ , and the spin functions  $\alpha, \beta$ , there is only one term in the  $P$ -summation which does not vanish. This is the leading diagonal term, and it gives (remembering that the  $\phi$ , are also normalized)

$$H_1 \equiv \int \phi_1^*(1) H^0(1) \phi_1(1) d\tau_1. \quad (100)$$

Thus  $H_1$  is the energy for the m.o.  $\phi_1$  in the core potential. The other terms in the first set in (99) give similar results, in which, on account of the spin, each  $H_r$  occurs twice. This part of the total energy reduces, therefore, to

$$2 \sum_{s=1} H_s, \quad (101)$$

where

$$H_s \equiv \int \phi_s^*(1) H^0(1) \phi_s(1) d\tau_1. \quad (102)$$

We have used the coordinates of electron 1 as current coordinates in (102), but since this is an integral over all space we could have used any other electron instead.  $H_s$  is a function, not of position, but of the m.o.  $\phi_s$ . It is more properly called a functional.

A typical member of the second set of terms in (99) is

$$\phi_1^*(1)\alpha^*(1) \dots \phi_n^*(2n)\beta^*(2n) \cdot \frac{1}{r_{si}} \cdot \sum_P (-1)^P \phi_1(1)\alpha(1) \dots \phi_n(2n)\beta(2n) d\tau^{2n}. \quad (103)$$

Let us first consider the term arising from  $1/r_{12}$ . Then, on account of the orthonormality of the spin orbitals, the only term in the  $P$  summation that is nonvanishing is the leading diagonal term, and the integral reduces to

$$\int \phi_1^*(1)\phi_1^*(2) \cdot \frac{1}{r_{12}} \cdot \phi_1(1)\phi_1(2) d\tau_1 d\tau_2 = J_{11}, \text{ say.}$$

The term arising from  $1/r_{13}$  is a little more complicated. Two terms in the  $P$  summation have to be considered. The integral reduces to:

$$\int \phi_1^*(1)\phi_2^*(3) \cdot \frac{1}{r_{13}} \cdot [\phi_1(1)\phi_2(3) - \phi_2(1)\phi_1(3)] d\tau_1 d\tau_2 = J_{12} - K_{12}$$

where, in general,

$$J_{ij} = \int \phi_i^*(1)\phi_j^*(2) \cdot \frac{1}{r_{12}} \cdot \phi_i(1)\phi_j(2) d\tau_1 d\tau_2, \quad (104)$$

$$K_{ij} = \int \phi_i^*(1)\phi_j^*(2) \cdot \frac{1}{r_{12}} \cdot \phi_i(1)\phi_i(2) d\tau_1 d\tau_2. \quad (105)$$

$J_{ij}$  is sometimes called the Coulomb integral for the orbitals  $\phi_i$ ,  $\phi_j$  and  $K_{ij}$  is the corresponding exchange integral.

The contribution of type (103) arising from  $1/r_{14}$  reduces to the single term

$$\int \phi_1^*(1) \phi_2^*(4) \cdot \frac{1}{r_{14}} \cdot \phi_1(1) \phi_2(4) d\tau_1 d\tau_4 = J_{12}.$$

All other terms follow in just the same way, and enable us to write (99) in the form

$$E = 2 \sum_{s=1}^n H_s + \sum_{s \neq t}^n (2J_{st} - K_{st}) + \sum_{s=1}^n J_{ss}.$$

Since  $J_{ss} = K_{ss}$ , this is equivalent to

$$E = 2 \sum_{\text{all } s} H_s + \sum_{\text{all } s, t} (2J_{st} - K_{st}) \quad (106)$$

This last equation is the fundamental one for all our later work in this chapter. It is, of course, identical in form to the equations for the energy of a single determinant wave function for an atom.

### 2.18 Hartree-Fock Equations

We shall now make use of (106) in two ways. In both we make use of the variation principle (Vol. I, Chapter 6) that the true wave functions are such as to make (106) stationary. In the first situation we imagine ourselves varying the complete set of molecular orbitals  $\phi_s$ , in the second (see § 2.18) we supposed that each  $\phi_s$  is expanded in an LCAO form, and we vary the sets of coefficients in these linear combinations.

Consider a particular  $\phi_s$ . Let it be modified to  $\phi_s + \delta\phi_s$ , always maintaining the orthonormality conditions  $\int \phi_s^* \phi_t d\tau = \delta_{st}$ . The first order variation in  $E$ , as given by (106) is now to be set equal to zero. Thus  $\delta E = 0$ . But the restrictive conditions implied by the orthonormality conditions are included by Lagrange multipliers. We require that the function

$$2 \sum_{\text{all } s} H_s + \sum_{\text{all } s, t} (2J_{st} - K_{st}) - \sum_{\text{all } s, t} \epsilon_{st} \left( \int \phi_s^* \phi_t d\tau - \delta_{st} \right) \quad (107)$$

shall be stationary, for unrestricted variations of each separate  $\phi_s$ . In (107) the last summation is a double one, over all values of  $s$  and  $t$ . We shall not work through the detailed analysis here (see, e.g., Roothaan<sup>23</sup>) but merely state the results as follows.

(1) As a result of the Hermitian character of the total Hamiltonian  $H$ , the matrix  $\epsilon$  is itself Hermitian; that is,

$$\epsilon_{ts} = \epsilon_{st}^* \quad (108)$$

(2) The differential equations satisfied by the  $\phi_s$  are given by

$$F(1)\phi_s(1) = \sum_i \phi_i(1)\epsilon_{is} \quad (109)$$

where  $F$  is a kind of effective one-electron Hamiltonian, that takes the form

$$F(1) = H^0(1) + G(1) \quad (110)$$

$H^0(1)$  will be recognized as the core Hamiltonian introduced in (96), and  $G(1)$  is a combined exchange and Coulomb operator defined by

$$G(1) = \sum_i [2J_i(1) - K_i(1)] \quad (111)$$

where, for any function  $\phi(1)$ ,

$$J_i(1)\phi(1) = \left[ \int \frac{\phi_i^*(2)\phi_i(2)}{r_{12}} d\tau_2 \right] \phi(1), \quad (112)$$

$$K_i(1)\phi(1) = \left[ \int \frac{\phi_i^*(2)\phi(2)}{r_{12}} d\tau_2 \right] \phi_i(1). \quad (113)$$

The operator  $J_i$  will be recognized as the potential field provided for electron 1 by the Coulomb repulsion due to electron 2 in the orbital  $\phi_i$ . The operator  $K_i$  has no simple physical counterpart, but is evidently an exchange potential energy operator.

(3) If we let  $\phi$  denote the row vector  $(\phi_1, \phi_2, \dots, \phi_n)$  the set of equations (104) can be put in the very simple matrix form

$$F\phi = \phi\epsilon. \quad (114)$$

These equations are the Hartree-Fock equations for the molecule. It will be noticed from the right-hand side of (109) that each equation involves every one of the  $\phi_i$  functions. They are therefore a set of coupled differential equations. On account of their complexity, it is not surprising that they have not yet been solved for any molecule more complicated than  $H_2$ .<sup>24</sup> However, we can see that the use of a one-electron Hamiltonian, as in earlier sections of this chapter, is not valid. It is equivalent either to deleting from (109) all the terms involving other orbitals than  $\phi_s$  or alternatively to replacing them by some invariable supposed equivalent.

## 2.19 Roothaan Equations

Our second application of (106) is to the LCAO approximation. We now suppose that each m.o.  $\phi_s$  may be expressed as a linear combination of atomic orbitals  $\psi_p$ . There will often — but by no means always — be one  $\psi_p$  for each atom. In general we shall write

$$\phi_s = \sum \psi_p c_{ps}. \quad (115)$$

The only variables now are the coefficients  $c_{ps}$ . But before we start varying these it is convenient to express some of our equations in matrix form. Let us write

$$\psi = (\psi_1, \psi_2, \dots, \psi_m) \quad (116)$$

$$c_s = \begin{pmatrix} c_{1s} \\ c_{2s} \end{pmatrix} \quad (117)$$

$$C = \begin{pmatrix} c_{11} & c_{12} & \dots & c_{1n} \\ c_{21} & c_{22} & \dots & c_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ c_{m1} & c_{m2} & \dots & c_{mn} \end{pmatrix} : (c_1, c_2, \dots, c_n) \quad (118)$$

Then

$$\phi_s = \psi c_s \quad (119)$$

and

$$\phi = \psi C. \quad (120)$$

Equation (119) deals with one molecular orbital, equation (120) with all of them at once. Now the individual  $\psi_p$  will not usually be orthogonal (though of course the  $\phi$  must be!). So we introduce the overlap matrix

$$S = ||S_{pq}|| \quad (121)$$

where

$$S_{pq} = \int \psi_p^* \psi_q d\tau. \quad (122)$$

Clearly  $S_{qp} = S_{pq}^*$ .  $S$  is therefore Hermitian. Usually, however, the  $\psi$  are real, and then so also is  $S$ .

We can now show that (106) takes the form

$$E = 2 \sum_s c_s^* H c_s + \sum_{\text{all } s, t} (2c_s^* J_t c_s - c_s^* K_t c_s) \quad (123)$$

where  $\mathbf{H}$  is the square matrix of order  $m$  given by

$$H_{pq} = \int \psi_p^*(1) H^0(1) \psi_q(1) d\tau_1 \quad (124)$$

and  $\mathbf{J}_t$ ,  $\mathbf{K}_t$  are square matrices, also of order  $m$ , given by (see Eqs. 112 and 113)

$$(J_t)_{pq} = \int \psi_p^*(1) J_t(1) \psi_q(1) d\tau_1, \quad (125)$$

$$(K_t)_{pq} = \int \psi_p^*(1) K_t(1) \psi_q(1) d\tau_1 \quad (126)$$

The variation of the coefficients  $\mathbf{C}$  must be made subject to the orthonormality conditions. These are

$$\begin{aligned} 1 &= \int \phi_i^* \phi_i d\tau = \mathbf{c}_i^* \mathbf{S} \mathbf{c}_i, \\ 0 &= \int \phi_i^* \phi_u d\tau = \mathbf{c}_i^* \mathbf{S} \mathbf{c}_u \quad (i \neq u). \end{aligned} \quad (127)$$

The incorporation of these conditions requires the introduction of Lagrange multipliers  $\epsilon_{is}$  as in § 2.17. Our final result can be put in the form:

$$\mathbf{F} \mathbf{c}_s = \sum_i \mathbf{S} \mathbf{c}_i \epsilon_{is} \quad (128)$$

In this equation  $\mathbf{F}$  is the matrix in the  $\psi$  representation with elements

$$F_{pq} = \int \psi_p^* F \psi_q d\tau \quad (129)$$

and defined exactly as in (110). We can combine all the set of Eqs. (128) in one single equation

$$\mathbf{F} \mathbf{C} = \mathbf{S} \mathbf{C} \boldsymbol{\epsilon}, \quad (130)$$

an equation which bears a close resemblance to (114), and would become identical with it in the limit when the set  $\psi_p$  became infinite in number and formed a complete set.

The difficulty in the use of (128) lies in the fact that it is not linear in the expansion coefficients  $c_{ps}$ . This is because, according to (110),  $\mathbf{F}$  involves the Coulomb and exchange potentials  $J_t$  and  $K_t$ , both of which are defined in the  $\phi$  scheme. When these are converted into the  $\psi$  scheme quadratic terms in  $c_{ps}$  will appear. Hence despite their simple appearance, the Eqs. (128) and (130) are actually of third degree in the unknown  $c_{ps}$ . They



are generally solved by the use of an electronic computer, making use of whatever symmetry exists in the molecule. This is exactly what was done in obtaining the SCF LCAO molecular orbitals for water, to which reference was made in § 2.14. Since this is an excellent example of the use of the Eqs. (128) we shall conclude with a brief description of this work in the form set out by Ellison and Shull.<sup>25</sup>

Let us use the notation of Fig. 13, and take into account all ten molecular electrons. In the separated atoms they would arise from  $O(1s^2 2s^2 2p_x 2p_y 2p_z)$ ,  $H_1(1s)$ ,  $H_2(1s)$ . On account of the symmetry, however, we may divide the orbitals into groups. Thus the first group contains only  $O(2p_z)$  since this is antisymmetric in the  $xy$ -plane, whereas all the others are symmetrical. This atomic orbital therefore remains almost unaffected by the formation of the molecule. The second group divides into those which are symmetrical in the  $xz$ -plane, viz.,  $O(1s)$ ,  $O(2s)$ ,  $O(2p_x)$  and the combination  $H_1 + H_2$ , and those which are antisymmetric in this plane, viz.,  $O(2p_y)$  and  $H_1 - H_2$ . Thus molecular orbitals are of the form

Group 1, $\pi$ orbitals, $O(2p_z)$	there is 1 of these
Group 2, $\sigma$ orbitals, symmetrical in $xz$	there are 4 of these
$c_1 O(1s) + c_2 O(2s) + c_3 O(2p_x) + c_4 (H_1 + H_2)$	
antisymmetrical in $xz$	there are 2 of these
$c_5 O(2p_y) + c_6 (H_1 - H_2)$	

The  $\pi$  orbital in group 1 has symmetry  $b_1$ , the symmetrical  $\sigma$  orbitals in group 2 have symmetry  $a_1$  and the antisymmetrical ones  $b_2$ . It appears, either on grounds of general plausibility, or by comparison with the simpler treatment in § 2.14, or by direct calculation, that all the seven m.o.'s are occupied in the ground state, except for the topmost orbitals in each of the  $\sigma$  groups. Ellison and Shull solved (128) in which the only nonvanishing  $c$ 's were those implied in the form of the orbitals just described. In all, there were no less than 14 undetermined coefficients to be determined, together with the corresponding energies. It will be realized that this represents a very considerable amount of numerical computation. The final results are that the occupied orbitals are

$\sigma$ orbitals	energy	symmetry
$1.000 O(1s) + 0.016 O(2s) + 0.002 O(2p_x) - 0.002 (H_1 + H_2)$	- 557.3 ev	$a_1$
$- 0.029 O(1s) + 0.845 O(2s) + 0.133 O(2p_x) + 0.126 (H_1 + H_2)$	- 36.19 ev	$a_1$
$- 0.026 O(1s) - 0.460 O(2s) + 0.828 O(2p_x) + 0.236 (H_1 + H_2)$	- 13.20 ev	$a_1$
$0.543 O(2p_y) + 0.548 (H_1 - H_2)$	- 18.55 ev	$b_2$
$\pi$ orbital: $O(2p_z)$	- 11.79 ev	$b_1$

where  $H_1$  and  $H_2$  are ordinary 1s orbitals of form  $\sqrt{(1/\pi)} e^{-r}$ , and the other atomic orbitals are all oxygen ones defined by

$$\begin{aligned} O(1s) &= \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha r}, & O(2p_z) &= \sqrt{\frac{\beta^5}{\pi}} x e^{-\beta r}, \\ O(2s) &= \frac{\sqrt{\frac{\beta^5}{3\pi}} r e^{-\beta r} - 0.233 O(1s)}{0.973}, \text{ etc.,} \end{aligned}$$

with  $\alpha = 7.7$ ,  $\beta = 2.275$ . The peculiar form of  $O(2s)$  is chosen because it is orthogonal to  $O(1s)$ .

Once we know the wave function we can calculate any other quantities that we desire from it. But we shall not describe these here. It is sufficient to have shown that by a technique of this kind it is possible to determine these SCF orbitals, and that such calculations are vastly more complex for a molecule than for an atom.

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## 4. Molecular Spectra

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The problems encountered in the interpretation of molecular spectra form some of the most satisfying examples of the application of the quantum theory. Possibly this arises from the fact that they are sufficiently simple to be solvable, sufficiently complex to be interesting, and so well-documented by experimental data as to be readily verified.

The total extent of the field of molecular spectra is large and it would not be possible, within the scope of the present book, to present more than a judicious sampling. Many interesting aspects have been omitted. These include a discussion of Raman spectra, of Fermi resonance, of the finer details of the vibration and rotation interactions in polyatomic molecules, of hindered rotation, and of the qualitative description of large molecules. In addition to these, omission is necessarily made of the great wealth of data and interpretation for the many individual molecules which have been

investigated. The student will find the books or reviews by Herzberg,<sup>1</sup> Dennison,<sup>2</sup> Townes and Schawlow<sup>3</sup> and Wilson *et al.*<sup>4</sup> helpful in pursuing the subject further.

## 1. General Considerations

At first sight it appears somewhat paradoxical that a molecule containing  $n$  electrons and  $N$  nuclei should furnish a fruitful example for the application of the quantum theory. The system, even excluding spins, is one of  $3(n + N)$  degrees of freedom and hence would seem to be beyond the capabilities of any existing mathematical means of solution. This statement is correct if an exact solution is required, nevertheless, it will be shown that approximate solutions of excellent accuracy may be obtained. The key lies in the fact that the Hamiltonian, to a high order of approximation, separates into the sum of four functions, the first of which depends only upon coordinates of the electrons relative to the nuclei, the second upon the coordinates of the nuclei relative to each other, the third upon coordinates describing the rotation of the entire system, and the fourth upon translational coordinates. This latter function has no bearing on the problem of molecular spectra and consequently will be ignored. Thus  $H \cong H_e + H_{\text{vib}} + H_{\text{rot}}$ .

A proof of the approximate separation of the Hamiltonian has been given by Born and Oppenheimer<sup>5</sup> using an expansion in powers of the ratio the electron and proton masses. An essential reason for the separation may be traced to the fact that the characteristic frequencies to be associated with the motions of the electrons and of the nuclei are of a different order of magnitude. The following qualitative considerations may be helpful. In the first place the forces acting both upon the electrons and upon the nuclei are due principally to the electrostatic forces between elementary charges over distances of the order of the dimension of a molecule, namely, a few angstrom units. Thus the forces on both types of particle are essentially the same. The characteristic frequencies will then stand in the ratio of  $(M/m)^{1/2}$  where  $M$  and  $m$  are the masses of a nucleus and an electron respectively. In the least favorable case, namely when the nucleus is a proton, this ratio has a value of about 43. Experimental observations bear out these considerations at least, qualitatively, since the electronic frequencies of molecules and atoms are of the order of the Rydberg constant, that is, around  $100,000 \text{ cm}^{-1}$  while the vibrational bands associated with the motion of protons occur in the neighborhood of  $3000 \text{ cm}^{-1}$ . It is a well-known property of periodic systems that motions of widely different frequencies

are nearly additive and that interaction terms are ineffectual in coupling them.\*

A qualitative classical way of describing the situation is to note that the nuclei are subjected to forces arising from the mutual interaction of their electric charges and also from the charges of the electrons. These latter are in rapid periodic motion around the nuclei (classical picture) and hence contribute effects due mainly to averages over their positions. To the nuclei, the electrons appear to be an averaged charge distribution while to the electrons, during any one period of their motion, the nuclei appear to be stationary. From these considerations as well as from the more exact discussion by Born and Oppenheimer, the conclusion is reached that the original Hamiltonian may be split into the sum of a Hamiltonian containing the electron coordinates and a Hamiltonian describing the vibration and rotation of the nuclei.

This latter Hamiltonian further separates, approximately at least, into a vibration Hamiltonian involving the mutual coordinates of the nuclei and a rotational Hamiltonian giving the rotation of the molecule. This separation again may be understood on the basis of the different orders of magnitude of vibration and rotational frequencies. Thus in a typical molecule such as HCl, the vibration frequency (expressed in waves per cm) is observed to lie at approximately  $3000\text{ cm}^{-1}$ . The rotational frequencies are, in round numbers,  $20j\text{ cm}^{-1}$  where  $j$  is the rotational quantum number. At room temperature in thermal equilibrium the most probable value of  $j$  lies between 3 and 4 and there are exceedingly few molecules with  $j$  higher than 15. For these latter the ratio of vibration to rotation frequencies would be 10.

\* The following highly simplified system illustrates this point. Consider a large mass  $M$  (a nucleus) which may move along a line and which is attached to a fixed point (the remainder of the molecule) by a spring having a spring constant  $k$ . A second mass  $m$  (an electron) which may move along the same line is attached to the mass  $M$  by a spring identical to the first spring (assumption of equal forces between nuclei and electrons). This system may be solved by the usual method of normal vibrations and since all motions are simple harmonic the results of a classical theory treatment will be identical with those of the quantum theory. It is easily shown that there will exist two frequencies  $\nu_1$  and  $\nu_2$  which may be expressed by means of a power series in  $m/M$ .

$$\nu_1 = (1/2\pi)(k/m)^{1/2} (1 + m/2M + \dots) \quad \text{and} \quad \nu_2 = (1/2\pi)(k/M)^{1/2} (1 - m/2M + \dots).$$

Since  $(1/2\pi)(k/m)^{1/2}$  is clearly the frequency of the electron under the conditions of a fixed nucleus and  $(1/2\pi)(k/M)^{1/2}$  is the frequency of the nucleus ignoring the existence of the electron, it is seen that the actual frequencies are altered through the coupling of the nucleus and electron by corrections of magnitude  $m/2M$ , i.e., of the order of one part in 4000.

As a further aspect of the problem it is instructive to compare the amplitude of the vibratory motion of the nuclei with normal distances between nuclei. It may be shown (cf. Vol. I, Chapter 3, § 2) that a particle,  $m$ , undergoing simple harmonic motion has a wave function (and hence a positional probability) which is primarily confined to a region  $\pm [(2n + 1) \hbar / 4\pi^2 m \nu_0]^{1/2}$ , where  $n$  is the vibrational quantum number. This region corresponds exactly to the amplitude of oscillation of a classical particle. Again taking HCl as an example, a substitution shows that the amplitude is  $0.106 (2n + 1)^{1/2} \times 10^{-8}$  cm. The equilibrium distance between the H and Cl nuclei as determined from the fine structure spacing is  $1.27 \times 10^{-8}$  cm. Thus in the normal and low excited states of the molecule the vibrational amplitude is of the order of 1/10 the distance between the nuclei. It is thus quite rational to approximate the system by a rotator and an oscillator. The interaction (which will be explicitly calculated for the diatomic molecule) is feeble since to the rotator the rapid oscillatory motion over a small amplitude virtually averages its effects to zero, while to the oscillator the centrifugal forces due to the slow rotational motion are almost negligible.

The qualitative picture of a molecule which has been given is important in setting up the mathematical framework for a more exact description. In summarizing one may say that in discussing the electrons the nuclei may be considered to be fixed. In discussing the motion of the nuclei, the effect of the electrons may be replaced by a potential which is a function of the positions of the nuclei. If the molecule is stable, the potential function for the nuclei possesses minima which determine their equilibrium positions. The nuclei may oscillate about these equilibrium positions but the amplitude of oscillation (extent of their wave functions) is small in comparison with the distances between the equilibrium positions. Thus, as a whole, the molecule has a semirigid structure which may undergo rotations. In the next section the diatomic molecule will be considered in some detail and in the succeeding section a number of typical polyatomic molecules will be discussed.

## 2. Diatomic Molecules

### 2.1 Electronic Levels

As has already been shown the large difference in mass between electrons and nuclei, coupled with the fact that the long range forces between electrons and nuclei are of essentially the same magnitude, insures that the Hamiltonian, to a high order of approximation, splits into two terms. The first of these relates to the problem of electrons moving in the field of nuclei

which are fixed in space while the second describes the problem of nuclei bound together by forces arising from the averaged effects of the electrons. In the present section the first of these Hamiltonians will be considered for the special case of a diatomic molecule.

Let it be supposed that the two nuclei are separated by the distance  $r$  and are held fixed. The quantity  $r$  is not necessarily the equilibrium distance but may have any assigned value from zero to infinity. The potential entering the Hamiltonian arises from the coulomb repulsions between the electrons and from the coulomb attractions of the electrons to each of the nuclei. It also includes the potential of the nuclei relative to each other but since their positions are fixed this enters as a constant parameter. Clearly the potential energy will be unaffected if the entire system of electrons is rotated through an angle about the line joining the two nuclei. A similar remark holds for the kinetic energy of the electrons and consequently the entire Hamiltonian must be independent of the angle  $\phi$  although it will contain the canonically conjugate momentum  $p_\phi$ . Since  $\phi$  is a cyclic coordinate it follows that  $p_\phi$ , the orbital angular momentum along the line joining the nuclei, is a constant of the motion and possesses eigenvalues  $\pm \Lambda \hbar$  where  $\Lambda = 0, 1, 2, 3, \dots$ . It has proved convenient to classify the electronic states by means of  $\Lambda$  and the designations  $\Sigma, \Pi, \Delta, \Phi, \dots$  are used for  $\Lambda = 0, 1, 2, 3, \dots$  respectively. Of course for any given value of  $\Lambda$ , there will exist many different energy states which, in general, may be widely separated.

The present situation may be compared and contrasted with that of an atom containing one nucleus and a number of electrons. In this latter case the potential energy possesses spherical symmetry and the Hamiltonian can not depend upon the space orientation of the system. This leads to a conservation of orbital angular momentum whose square has the eigenvalues  $(L^2 + L)\hbar^2$  where  $L$  is an integer including zero. The electronic levels are classified by means of  $L$  and are designated as  $S, P, D, F, \dots$  states according as  $L = 0, 1, 2, 3, \dots$ . In the presence of an external field (for example, an electric field), the component of the angular momentum along the field axis is likewise a constant of the motion, and is denoted by  $\pm M_L \hbar$ . For any given  $L$ ,  $M_L$  may take the values  $0, 1, 2, \dots, L$ . Clearly the existence of the external field converts the spherical symmetry of the free atom to a field of axial symmetry and consequently  $M_L$  and  $\Lambda$  are identical quantities.

The condition of axial symmetry imposes certain general restrictions on the wave functions and selection rules. Let the position of the  $i$ th electron be designated by the cylindrical coordinates  $(z_i, r_i, \phi_i)$  where  $z_i$  is the distance along the symmetry axis and  $\phi_i$  the azimuthal angle about it. From the

conservation of angular momentum along the symmetry axis it follows that the wave function has the rigorous form,

$$\psi = \chi e^{iA\phi} \quad \text{or} \quad \bar{\chi} e^{-iA\phi} \quad (1)$$

in which  $\chi$  and  $\bar{\chi}$  are functions of  $(z_1, r_1, \phi_1), \dots (z_n, r_n, \phi_n)$  where  $n$  is the number of electrons and  $\chi(-\phi_i) = \bar{\chi}(\phi_i)$ . The azimuthal angle,  $\phi$ , corresponds to a rotation of the entire system about the symmetry axis.

Let the cartesian coordinates  $x, y, z$  be introduced where the  $z$ -axis coincides with the axis of the system. The electric moment will have the components  $\mu_x = e\Sigma x_i$ ,  $\mu_y = e\Sigma y_i$  and  $\mu_z = e\Sigma z_i$ .  $\mu_x$  and  $\mu_y$  will clearly depend upon the total azimuthal angle  $\phi$  by means of the factors  $\sin \phi$  and  $\cos \phi$  (with proper choice of the reference plane for  $\phi$ ), while  $\mu_z$  must be independent of  $\phi$ . A calculation of the matrix elements of the electric moment will yield certain general properties since the variables  $\phi$  must be integrated from 0 to  $2\pi$ . Clearly in the case of either  $\mu_x$  or  $\mu_y$ , the initial and final states must be characterized by values of  $A$  which differ by unity. In the case of  $\mu_z$  however  $A$  must be the same for the two states. The selection rules  $\Delta A = \pm 1$  or 0 have therefore been established. Thus returning to the classification of electronic states, transitions of the type  $\Sigma \rightarrow \Sigma$ ,  $\Pi \rightarrow \Pi$ ,  $\dots \Sigma \rightarrow \Pi$ ,  $\Pi \rightarrow \Delta$ ,  $\dots$  may occur but not the transitions  $\Sigma \rightarrow \Delta$ ,  $\dots$ .

The spin of the electrons introduces modifications for a diatomic molecule which are similar to those for an atom. Let the resultant of all the electronic spin angular momenta be given by the quantum number  $S$  which is either an integer or an half odd integer depending on whether the number of electrons is even or odd. Since the spins are not affected by an electric field but only by a magnetic field, the  $A = 0$  states are unchanged by  $S$ . When  $A \neq 0$ , however, there exists an orbital angular momentum and consequently a magnetic field whose axis coincides with the symmetry axis. The spin  $S$  may then orient itself in  $2S + 1$  ways relative to it. Let the component of  $S$  along the axis be denoted by  $\Sigma$  (not to be confused with the electronic states where  $A = 0$  which are called  $\Sigma$  states). The total angular momentum along the symmetry axis is  $\Omega\hbar$  where  $\Omega = |A + \Sigma|$ . Since the different relative orientations of  $S$  will result in different amounts of magnetic coupling energy (assuming that  $A \neq 0$ ) each orbital state now becomes a multiplet with  $2S + 1$  levels. The splittings within a multiplet are generally small compared with the usual separations between the orbital terms and may range from a few to a few thousand waves per cm. The multiplicity is designated by a left superscript, thus  $^3\Pi$  denotes a multiplet for which  $A = 1$  and  $S = 1$ . The individual components of the multiplet are distin-



guished by a subscript equal to  $\Lambda + \Sigma$ . In the case presented these would be  ${}^3\Pi_2$ ,  ${}^3\Pi_1$  and  ${}^3\Pi_0$ .

Up to this point the nuclei of the diatomic molecule have been considered as fixed, the distance between them being the constant  $r$ . The energy of the system,  $E$ , in a given state will contain two terms, the eigenvalue of the electrons and the coulomb interaction between the nuclei. Both of these terms depend upon the value of the internuclear distance  $r$  which has been chosen, the former in a very complicated manner and the latter as  $1/r$ .

By choosing different values for  $r$ , the energy may be represented as a function of that parameter and one obtains  $E(r)$ . In Fig. 1 a number of the

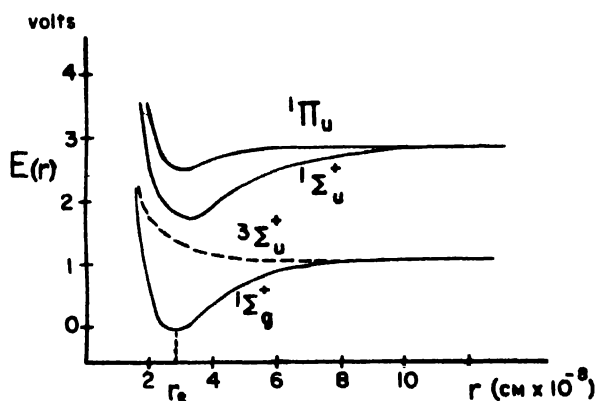


FIG. 1. Electronic energy levels of the  $\text{Li}_2$  molecule (after Mulliken<sup>6</sup>).

electronic energy levels of the  $\text{Li}_2$  molecule are plotted against  $r$ . In principle, curves of this type could be computed through a knowledge of the number, charge, and mass of the electrons and the charges of the nuclei. Although progress has been made in this direction through the use of electronic computers, for all except the simplest molecules, the curves must be established by means of the observed spectrum.

As mentioned earlier, the Hamiltonian of the entire system, electrons and nuclei, to a high order of approximation divides into two terms. In the first of these the nuclei are held fixed and the electrons move in the resulting field. The second term describes the motion of the nuclei in the averaged field produced by the electrons. The coordinates are those of the nuclei and will describe their vibration and rotation. The potential is the energy of the system of electrons and consequently for the diatomic molecule is just the function  $E(r)$ . The lowest curve shown in Fig. 1 represents the normal electronic state. Since it possesses a minimum, the molecule has a stable

equilibrium configuration in which the nuclei are separated by  $r_e$ . The curvature of  $E(r)$  at  $r = r_e$  together with the masses of the nuclei, determines the frequency  $\nu_e$  of infinitesimal oscillation. As a first approximation it fixes the spacing of the vibrational energy levels. Towards the origin,  $E(r)$  rises steeply indicating strong repulsion, while for large  $r$  the force between the nuclei decreases to zero since the potential approaches a horizontal asymptote corresponding to two separated Li atoms.  $E(r = \infty) - E(r_e)$  is closely equal to the energy of dissociation — the actual energy is slightly lower due to the zero-point energy of vibration.

The second curve in Fig. 1 possesses no minimum and the force between the nuclei is always repulsive. This electronic state does not lead to a stable molecule. The higher curves shown in the same figure do have stable equilibrium configurations. The equilibrium distances for these excited electronic states do not coincide with that of the normal state and are in general somewhat larger.

## 2.2 Vibration-Rotation Levels

Consider now the second term of the Hamiltonian which describes the two nuclei moving under a potential  $V(r) = E(r)$  produced by the averaged effects of the electrons. For simplicity, let the electronic state be  $^1\Sigma$ , that is, the electrons possess neither a resultant orbital nor spin angular momentum. This system belongs to the category of two-body central force problems already treated in Vol. I, Chapter 3, § 3, and a separation between relative motion and motion of the centre of gravity may be effected in the usual manner. The relative motion may be described by means of the spherical coordinates  $(r, \theta, \phi)$  where  $r$  is the distance between the two nuclei. The wave function has, as for all problems of this class, the form

$$\psi = R(r) P_j^m(\cos \theta) e^{\pm im\phi} \quad (2)$$

where  $P_j^m(\cos \theta) e^{\pm im\phi}$  are surface harmonics. The square of the total angular momentum is  $(j^2 + j)\hbar^2$  while its component along the polar axis of the coordinate system is  $\pm m\hbar$ .  $j$  and  $m$  may assume all positive integral values including zero but  $m \leq j$ .

The differential equation defining the radial part of the wave function becomes somewhat simpler by introducing  $U(r) = rR(r)$  in which case it has the form

$$\frac{d^2 U}{dr^2} + \left( \frac{2\mu}{\hbar^2} \right) \left[ E - V(r) - \frac{(j^2 + j)\hbar^2}{2\mu r^2} \right] U = 0 \quad (3)$$

where  $\mu$  is the reduced mass of the nuclei and equal to  $M_1 M_2 / (M_1 + M_2)$ . The eigenvalue  $E$  represents the combined energy of vibration and rotation.

The potential energy,  $V(r)$ , has the general form shown in Fig. 1 but is usually not known in detail. Two methods of attack have been employed. In the first of these  $V(r)$  is expanded about its minimum, namely the point where  $r = r_e$ , and the radial equation solved by successive approximation. The second method, which will be discussed later, consists in choosing a function for  $V(r)$  which has the proper form and for which an exact solution may be found.

For the approximation method it will be advantageous to use as variable the displacement from equilibrium,  $q = r - r_e$ . Developing, the potential becomes,

$$V = V_0 + \frac{1}{2} \left( \frac{d^2V}{dq^2} \right)_0 q^2 + \frac{1}{3!} \left( \frac{d^3V}{dq^3} \right)_0 q^3 + \frac{1}{4!} \left( \frac{d^4V}{dq^4} \right)_0 q^4 + \dots \quad (4)$$

The constant  $V_0$  may be absorbed into  $E$ , in which case the eigenvalues of  $E$  will have as their origin the minimum of the potential curve.

The first significant term in the development, namely,  $1/2(d^2V/dq^2)_0 q^2$  may be identified as the zeroth-order approximation. A mechanical system with kinetic energy  $\frac{1}{2}\mu\dot{q}^2$  and potential energy  $\frac{1}{2}kq^2$  represents an harmonic oscillator whose frequency  $\nu_e = (1/2\pi)(k/m)^{1/2}$ . Making the appropriate identification it is clear that  $\frac{1}{2}(d^2V/dq^2)_0$  may be replaced by  $2\pi^2\mu\nu_e^2$ .

The so-called centrifugal potential  $(j^2 + j)\hbar^2/2\mu r^2$  may also be expanded about the equilibrium point and becomes,

$$\frac{(j^2 + j)\hbar^2}{2\mu(r_e + q)^2} = \frac{(j^2 + j)\hbar^2}{2I_e} \left( 1 - \frac{2q}{r_e} + \frac{3q^2}{r_e^2} \dots \right) \quad (5)$$

where  $I_e = \mu r_e^2$  is the moment of inertia of the molecule in its equilibrium state.

The problem now may be described as a zeroth-order approximation system with radial equation,

$$\frac{d^2U}{dq^2} + \frac{2\mu}{\hbar^2} \left[ E_0 - 2\pi^2\mu\nu_e^2 q^2 - \frac{(j^2 + j)\hbar^2}{2I_e} \right] U = 0 \quad (6)$$

to which are added first- and second-order approximations to the potential

$$\begin{aligned} \lambda V_1 &= \frac{1}{3!} \left( \frac{d^3V}{dq^3} \right)_0 q^3 - \frac{(j^2 + j)\hbar^2 q}{I_e r_e}, \\ \lambda^2 V_2 &= \frac{1}{4!} \left( \frac{d^4V}{dq^4} \right)_0 q^4 + \frac{3(j^2 + j)\hbar^2 q^2}{2I_e r_e^2}. \end{aligned} \quad (7)$$

The zeroth-order radial equation is easily recognized as the standard wave equation of an harmonic oscillator,\* where however the usual energy constant has been augmented by the constant term  $-(j^2 + j)\hbar^2/2I_e$ . The solution is, (cf. Vol. I, Chapter 3, § 2)

$$E_0 = h\nu_e(n + \frac{1}{2}) + \frac{(j^2 + j)\hbar^2}{2I_e} \quad n = 0, 1, 2, \dots \quad (8)$$

$$U = \frac{H_n(x) e^{-x^2/2}}{\pi^{1/4} (2^n n!)^{1/2}} \quad \text{where} \quad x = \sqrt{2\pi\mu\nu_e/\hbar} q, \quad (9)$$

in which  $H_n(x)$  is the  $n$ th Hermitian polynomial.

Knowing the zeroth-order wave functions and energies, the first- and second-order changes in the energy,  $\lambda E_1$ , and  $\lambda E_2$  may be evaluated using the standard perturbation theory technique (Vol. I, Chapter 5, § 2.2 and § 2.4). It may be remarked that  $\lambda E_1 = 0$  since  $\lambda V_1$  is an odd function of  $q$  and since  $U^*U$  is an even function and consequently  $\int_{-\infty}^{\infty} U^* \lambda V_1 U dq = 0$ .

The results of applying perturbation theory through second-order are as follows. It is convenient to divide  $E$  by  $hc$  and thus express all quantities in waves per centimetre. A constant additive term is also introduced by the perturbation but since it has no influence upon the spectrum it has been omitted.

$$\frac{E}{hc} = \omega_e(n + \frac{1}{2}) + B_e(j^2 + j) - \omega_e x(n + \frac{1}{2})^2 - \alpha_e(n + \frac{1}{2})(j^2 + j) - D(j^2 + j)^2 \quad (10)$$

where

$$\begin{aligned} \omega_e &= \frac{\nu_e}{c}, \quad B_e = h/8\pi^2 c I_e, \\ \alpha_e &= - \left( \frac{h^2}{32\pi^4 c \nu_e I_e^2} \right) \left[ \left\{ r_e \left( \frac{d^3 V}{dq^3} \right)_0 / 4\pi^2 \mu \nu_e^2 \right\} + 3 \right], \\ \omega_e x &= \left( \frac{h}{192\pi^2 \mu c} \right) \left[ 5 \left\{ \left( \frac{d^3 V}{dq^3} \right)_0^2 / (4\pi^2 \mu \nu_e^2)^2 \right\} - 3 \left\{ \left( \frac{d^4 V}{dq^4} \right)_0 / 4\pi^2 \mu \nu_e^2 \right\} \right], \\ D &= h^3/128\pi^6 c \nu_e^2 I_e^3. \end{aligned} \quad (11)$$

\* Properly speaking there exists a difference in the boundary conditions. In the standard harmonic oscillator the wave function must vanish for  $q = \pm \infty$ . In the present equation however the wave function must vanish at the extreme limits of the coordinate, namely,  $-q = -r_e$  and  $+\infty$ . Since  $r_e$  is so much larger than the region in which the wave function has an appreciable value (the classical amplitude of vibration) and since the simple harmonic wave function falls off so very rapidly for large absolute values of the coordinate, it will be virtually zero at  $q = -r_e$ . In principle this difference in the boundary conditions could be corrected through a perturbation treatment but the net effect on the eigenvalues would be unobservable.

The expression for  $E/hc$  may be readily interpreted by noting that it is in the form of a power series expansion in the vibrational and rotational quantum numbers  $n$  and  $j$ . The first two terms represent respectively the energies of an harmonic oscillator and of a rigid rotator with moment of inertia  $I_e$ . The third term contains only the vibrational quantum number and expresses a change in the energy due to the anharmonicity of the potential, i.e., since the potential differs from parabolic form by reason of  $\lambda V_1$  and  $\lambda V_2$ . The fourth term contains both  $n$  and  $j$  and may be thought of in the following way. The rotation of the molecule and the consequent centrifugal force stretches the nuclei into a new position of equilibrium. The forces are here slightly altered due to the term  $\lambda V_1$  and to the centrifugal potential. Consequently the vibrational frequency and energy are changed. The last term contains only the rotational number  $j$ . As the molecule rotates its moment of inertia becomes larger and hence the rotational energy must fall. It is for this reason that the term in question is always negative. Since the balance is between the centrifugal force and, to first order, the harmonic part of the potential,  $2\pi^2\mu\nu_e q^2$ ,  $D$  does not contain the higher derivatives of  $V$ . It can be expressed as a function of  $\omega_e$  and  $B_e$ , namely  $D = 4B_e^3/\omega_e^2$ .

The molecular constants have been spectroscopically determined for several hundred diatomic molecules, often to a high degree of accuracy. In Table I a number of these sets of constants are listed for the purpose of exhibiting their orders of magnitude. The choice of molecules has been arbitrary except that it was desired to present examples ranging from very light to very heavy diatomic molecules. For convenience the numbers have been rounded to three or four significant figures.

TABLE I  
DIATOMIC MOLECULAR CONSTANTS (UNITS OF  $\text{cm}^{-1}$ )<sup>a</sup>

Molecule	$\omega_e$	$B_e$	$\omega_e x$	$\alpha_e$	$D_e$	$(D_e)_M$	$(\alpha_e)_M$
H <sub>2</sub>	4395	60.81	118	2.993	38,285	40,920	1.984
HCl	2989	10.59	52.0	0.302	37,225	42,950	0.274
N <sub>2</sub>	2360	2.010	14.4	0.019	79,890	96,700	0.017
CO	2170	1.931	13.5	0.017	90,705	87,200	0.017
K <sub>2</sub>	92.64	0.0562	0.354	$2.2 \times 10^{-4}$	4,190	6,060	$3.1 \times 10^{-4}$
I <sub>2</sub>	214.6	0.0374	0.613	$1.2 \times 10^{-4}$	12,550	18,780	$1.2 \times 10^{-4}$

<sup>a</sup> The experimental numbers are taken from G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. 1. Van Nostrand, New York, 1950.

The values of the centrifugal distortion constant  $D$  have been omitted since (1) they may be calculated from  $\omega_e$  and  $B_e$ , and (2) they are usually too small to be observable. In the case of  $N_2$ , for example  $D$  is computed to be  $6 \times 10^{-6} \text{ cm}^{-1}$ . In the lighter molecules  $D$  has been occasionally measured and found to be in good agreement with its predicted value. The last three columns of Table I will be discussed in the following paragraphs.

In contrast to the method of developing the potential and solving by successive approximation one may look for a potential function which has the correct general form and for which there exists an analytical solution. The only function so far discovered which allows a simple exact solution for both vibration and rotation, is the so-called ionic potential  $V = -(a/r) + (b/r^2)$ . Unfortunately the actual forces between the nuclei in a diatomic molecule appear to be of shorter range than those of the ionic potential. The results of the Heitler-London treatment of the  $H_2$  molecule (Chapter 3, § 2.3, in this volume) suggest that an exponential potential might be more suitable and this turns out to be correct.

The potential proposed by Morse is

$$V(r) = hcD_e [1 - \exp \{-\beta(r - r_e)\}]^2. \quad (12)$$

The first derivative

$$\frac{dV}{dr} = 2\beta hcD_e [\exp \{-\beta(r - r_e)\} - \exp \{-2\beta(r - r_e)\}]$$

is clearly zero for  $r = r_e$  and consequently  $r_e$  may be identified as the equilibrium distance between the nuclei.  $V(r = \infty) - V(r = r_e) = D_e hc =$  the equilibrium energy of dissociation. As remarked earlier, the actual energy of dissociation is slightly less since in the normal state the molecule possesses a zero-point vibrational energy. The constant  $\beta$  may be understood by setting  $(d^2V/dr^2)_{r=r_e} = 2\beta^2 hcD_e$  equal to its value in terms of the normal frequency and reduced mass, namely  $4\pi^2 \nu_e^2 \mu$ .

An exact solution of the radial equation may be obtained only for the rotationless state where  $j = 0$ . A second proviso is that the range of the variable is properly from  $-\infty$  to  $+\infty$  whereas in a radial equation  $r$  goes only from 0 to  $+\infty$ . In any actual case however, corrections due to a negative range for  $r$  would be entirely negligible. This arises from the fact that the Morse function is so very large at  $r = 0$  that, in effect, it may be replaced by  $\infty$  in which case the wave function vanishes for all negative values of  $r$ .\*

\* For example, substituting the appropriate constants for the HCl molecule, one obtains  $V(r = 0) = 130 D_e hc$ , that is, 130 times the energy of dissociation.

Substituting the Morse potential in the radial equation and setting  $= 0$ , one has

$$\frac{d^2 U}{dr^2} + \left( \frac{2\mu}{\hbar^2} \right) [E - hcD_e(1 - \exp\{-\beta(r - r_e)\})^2] U = 0. \quad (13)$$

Introducing the substitutions

$$\exp\{-\beta(r - r_e)\} = x, \quad \lambda^2 = \frac{2\mu(hcD_e - E)}{\hbar^2\beta^2} \quad \gamma^2 = \frac{2\mu hcD_e}{\hbar^2\beta^2} \quad (14)$$

the equation becomes,

$$x \frac{d^2 U}{dx^2} + x \frac{dU}{dx} + (-\lambda^2 + 2\gamma^2 x - \gamma^2 x^2) U = 0. \quad (15)$$

As  $r$  ranges from  $-\infty$  to  $+\infty$ ,  $x$  goes from  $\infty$  to 0. Near these limits an inspection of the equation shows that if  $U$  is to satisfy the boundary conditions, it must behave as  $e^{-\gamma x}$  and  $x^\lambda$  respectively. The indicated substitution  $U = x^\lambda e^{-\gamma x} F$  gives the equation,

$$x \frac{d^2 F}{dx^2} + (2\lambda + 1 - 2\gamma x) \frac{dF}{dx} + (2\gamma^2 - \gamma - 2\lambda\gamma) F = 0. \quad (16)$$

This equation may be solved by assuming a series expansion,  $F = \sum a_k x^k$ . The indicial equation in conjunction with the boundary condition for  $x = 0$  shows that  $k$  is positive and starts with  $k = 0$ . A substitution yields a two term recursion formula for  $a_k$ , namely

$$a_{k+1} = \frac{2\gamma k - (2\gamma^2 - \gamma - 2\lambda\gamma)}{(k+1)(k+2\lambda+1)} a_k. \quad (17)$$

An inspection of the series shows that  $F$  behaves as  $e^{2\gamma x}$  for large values of  $x$  unless the series terminates. This behavior would violate the boundary condition for  $x = \infty$ . The series will terminate at the  $k = n$  term providing

$$2\gamma^2 - 2\gamma - 2\lambda\gamma = 2\gamma n \quad \text{where} \quad n = 0, 1, 2, \dots \quad (18)$$

Setting in the values for  $\lambda$  and  $\gamma$ , one may readily solve for the energy. In contrast to the earlier treatment which used a perturbation expansion, the energy so obtained is exact, at least for the rotationless state  $j = 0$ :

$$\frac{E}{hc} = \omega_e(n + \frac{1}{2}) - \omega_e x(n + \frac{1}{2})^2 \quad (19)$$

where  $\omega_e = \nu_e/c = (D_e\beta^2 \hbar/2\pi^2\mu c)^{1/2}$  in accord with the earlier result and  $\omega_e x = \hbar\beta^2/8\pi^2\mu c$ . The rotational contributions may be obtained by merely adding those terms containing  $j$  as found from the earlier perturbation treatment.

The constants which are most readily obtained from the experimental spectrum are  $\omega_e$ ,  $\omega_e x$  and  $B_e$ . The Morse potential with its three parameters,  $D_e$ ,  $\beta$ , and  $r_e$  may be therefore evaluated. The following relations result from a direct substitution:

$$D_e = \frac{\omega_e^2}{4\omega_e x}$$

$$\alpha_e = \frac{6(\omega_e x B_e^3)^{1/2}}{\omega_e} \left[ 1 - \left( \frac{B_e}{\omega_e x} \right)^{1/2} \right] \quad (20)$$

This latter quantity may be obtained from the expression for  $\alpha_e$  which involved  $(d^3V/dr^3)_{r=r_e}$ . The last two columns in Table I give the values of  $D_e$  and  $\alpha_e$  calculated from these formulas. It will be noted that the calculated  $\alpha_e$  agree reasonably well with the corresponding observed values but the agreement for  $D_e$  is distinctly poorer. This is perhaps to be expected since  $\omega_e$ ,  $\omega_e x$ ,  $B_e$ , and  $\alpha_e$  are dependent upon the properties of  $V$  near the equilibrium configuration while  $D_e$  depends on the value of  $V$  for large values of  $r$ .

The energy of a diatomic molecule has been expressed as the sum of two terms, (1) the energy due to the electrons moving in the field of fixed nuclei, and (2) the vibration-rotation energy of the nuclei. This is of course only an approximation, although a very good one, and it is to be expected that there will exist interaction terms. The most important of these occur for those electronic states where there exists an orbital angular momentum along the internuclear direction, i.e., when  $\Lambda \neq 0$ . The spin angular momentum also couples to this axis giving a total component due to spin and orbital of  $\Omega$ . This situation is referred to as Hund's case (a). The angular momentum due to the rotation of the nuclei (with quantum number  $j$ ) combines with  $\Omega$  to give a total angular momentum (quantum number  $J$ ) with fixed direction in space about which each of the other vectors precess. The rotational energy to first order is  $B_e[J(J+1) - \Omega^2]$  in close analogy to a formula for the symmetrical top energy which will be discussed later.  $\Omega$  is directed along the internuclear axis but it may have two orientations, parallel or antiparallel. For the nonrotating molecule these have the same energy. When, however,  $j \neq 0$  the eigenstates built for the two possibilities do not have identical energies and each level is split into two, a phenomenon called  $\Lambda$  type doubling. The magnitude of the splitting increases with  $j$  and in most cases is small, of the order of a few tenths of a wave per centimetre.



## 2.3 Spectra of Diatomic Molecules

It will be convenient to divide the spectra into two classes, those which do not make a change in electronic state and those which do. The former presents many simple features and will be discussed first. The energy expression has already been given, (10), and it only remains to ascertain the allowed transitions. The transition probability (Vol. I, Chapter 8, § 5.1.4) is proportional to the sums of the squares of the matrix elements of the components of the electric dipole moment along the coordinate axes. These components are,

$$\begin{aligned} M_x &= \mu(r) \sin \theta \sin \phi, \\ M_y &= \mu(r) \sin \theta \cos \phi, \\ M_z &= \mu(r) \cos \theta \end{aligned} \quad (21)$$

where  $\mu(r)$  is the dipole moment along the internuclear axis. It is, of course, an unknown function of the internuclear distance. It will prove fruitful to develop it in the neighbourhood of the equilibrium distance  $r_e$ :

$$\mu(r) = \mu_e + \left( \frac{d\mu}{dr} \right)_{r_e} (r - r_e) + \frac{1}{2} \left( \frac{d^2\mu}{dr^2} \right)_{r_e} (r - r_e)^2 + \dots \quad (22)$$

The constant  $\mu_e$  is the permanent dipole moment of the molecule

The wave function separates into products of functions as shown in (2) and consequently the integrations over each of the three coordinates may be made independently. Consider the  $r$  integral,

$$R_i^* \mu(r) R_f r^2 dr \quad (23)$$

where  $R_i$  and  $R_f$  are the radial functions of the initial and final states. Using the development for  $\mu(r)$ , it is clear that the first term gives zero unless the initial and final states are identical since the radial wave functions form an orthonormal set. Using  $n$  for the vibrational quantum number, one concludes that transitions where  $\Delta n = 0$  may occur and that their transition probability is proportional to  $\mu_e^2$ .

In lowest order of approximation the radial function given by (3) and (9) is essentially that of a simple harmonic oscillator. The second term of (22) may be written as a constant times  $x$ , the variable of (9). The matrix elements of  $x$  vanish unless  $\Delta n = \pm 1$  (Chapter 2, Eq. 3). This transition gives rise to a frequency which, in zeroth-order at least, is just equal to the vibrational frequency  $\nu_e$ . In higher orders of approximation the matrix

elements of  $\mu(r)$  for which  $\Delta n = \pm 2, \pm 3$ , etc., do not vanish but they are small and thus lead to the prediction that the overtone bands, located at approximately  $2\nu_e, 3\nu_e, \dots$  will be weak, a prediction which is borne out by observation.

The remaining factors of  $M_x, M_y$  and  $M_z$ , namely  $\sin \theta \sin \phi, \sin \theta \cos \phi$  and  $\cos \theta$  are common to all two-body problems and from the properties of the surface harmonic functions it may be shown that they vanish\* unless  $\Delta j = \pm 1$ .

Using the above selection rules the spectral lines may be calculated from the energy expression of (10),

$$\left(\frac{\nu}{c}\right)_{n,j \rightarrow n - \Delta n, j - 1} = [\omega_e - \omega_e x(1 + 2n - \Delta n)]\Delta n + \quad (24)$$

$$[2B_e - \alpha_e(1 + 2n - \Delta n)]j - \alpha_e j^2 \Delta n - 4Dj^3$$

These lines constitute the so-called positive or *R* branch. The corresponding *P* branch lines  $(\nu/c)_{n,j-1 \rightarrow n - \Delta n, j}$  are given by an identical formula except that the signs of the terms proportional to  $j$  and  $j^3$  are changed to  $-$  and  $+$  respectively. It is therefore clear that the lines of both branches may be given by a single expression where  $j$  is replaced by an ordinal number  $m$  which assumes positive integral values for the *R* branch and negative integer values for the *P* branch. The value  $m = 0$  is excluded.

An inspection of (24) shows that the far infrared spectrum, where  $n = \Delta n = 0$ , will consist of the lines  $\{2B_e - \alpha_e\}j - 4Dj^3$ . Since  $D$  is a very small constant the lines are nearly equidistant. These lines as well as those in the near infrared are almost always observed in absorption rather than in emission. This introduces no change in their positions; however the actual transition is in the reverse direction, as,  $n, j \leftarrow n - \Delta n, j - 1$ .

The lines of the fundamental vibration band where  $\Delta n = 1$  and where, as is usually the case, the lowest vibration state is the ground state are given by,

$$\omega_e - 2\omega_e x + (2B_e - 2\alpha_e)m - \alpha_e m^2 - 4Dm^3 \quad \text{where} \quad m = \pm 1, \pm 2, \dots$$

Since for actual molecules  $B_e$  is larger than  $\alpha_e$ , the lines are approximately linearly spaced but they will show some convergence due to the term  $-\alpha_e m^2$ .

\* In the above discussion it has been tacitly assumed that the electronic state is a  $\Sigma$  state where the orbital angular momentum of the electrons along the internuclear axis  $\Lambda = 0$ . This is the case for the great majority of diatomic molecules in their lowest electronic states. If however  $\Lambda \neq 0$ , the transition  $\Delta j = 0$  is allowed, giving rise to what is called a *Q* branch. This obtains for the molecule NO.

As an example the fundamental vibration band of CO as observed by Whitcomb and Lagemann is given in Fig. 2.

Finally, consider a transition where a change occurs not only of the vibration and rotation energy but also of the electronic energy. These bands which are usually observed in emission are very complex indeed. The molecular constants of the upper state will be designated by single primes, thus  $E'_e$ ,  $\omega'_e$ ,  $\omega'_e x'$ ,  $B'_e$ , and those of the lower state by double primes.  $E'_e$  is the energy constant associated with the electrons moving in the field of fixed nuclei.  $(E'_e - E''_e)/h$  will be written as  $\nu_{e1}$ , and is the frequency associated with the electronic terms alone.

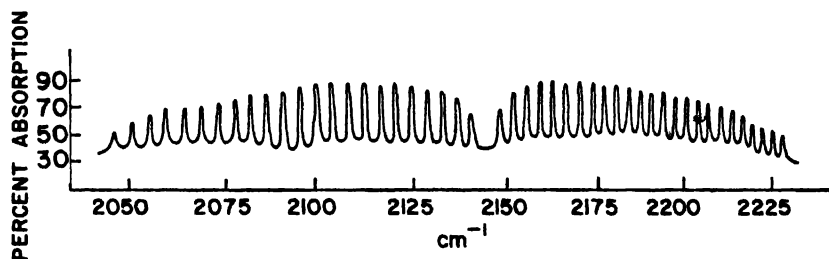


FIG. 2 The fundamental vibration band of the CO molecule (Whitcomb and Lagemann<sup>7</sup>).

The selection rules for  $J$  are unchanged for a transition between two electronic  $\Sigma$  states and are namely  $\Delta J = \pm 1$ . When one or both of the electronic states possesses an electronic orbital angular momentum however, i.e., when  $\Lambda \neq 0$ ,  $\Delta J = \pm 1$  or 0 and consequently the rotational lines form  $Q$  as well as  $P$  and  $R$  branches.

The change of vibrational number  $n' - n'' = \Delta n$  may have any value. This was also the case for the infrared vibration bands which do not involve any change in electronic state but there is one important difference. In the vibration bands discussed earlier, the fundamental band where  $\Delta n = 1$  was strong while the overtones  $\Delta n = 2, 3$ , etc., were successively much weaker. This situation came about since the zeroth approximation — and usually a very good approximation — of the vibrational Hamiltonian was that of a simple harmonic oscillator for which only the transition  $\Delta n = 1$  is allowed. In the case of an electronic transition the vibrational wave functions of each state may still be approximated by simple harmonic oscillator wave functions but both the frequencies and also the centres of the wave functions (i.e., the equilibrium distances) are different. The magnitude of the dipole matrix element will depend to a large extent upon the overlap of the two wave functions. These considerations were first treated qualitatively

by Franck and Condon and have subsequently been placed on a quantitative basis. The results may be stated in the following way. While all values of  $\Delta n$  are allowed, those values are particularly favoured where the largest values of the vibrational wave function of the upper electronic state most nearly coincide in internuclear distance with those of the lower electronic state. These largest values for a simple harmonic oscillator occur near the positions of the extremes of the motion of the corresponding classical mechanical oscillator.

Using the selection rules the positions of the lines may be readily calculated from energy expressions for the upper and lower states of the form shown in (10).

As a typical example, consider the transition  $n' \rightarrow n''$   $j \rightarrow j - 1$ . For simplicity the small terms involving the centrifugal stretching constant  $D$  have been neglected.

$$\begin{aligned} \nu_{n',j \rightarrow n'',j-1} = & \frac{\nu_{el}}{c} + \omega'_e(n' + \tfrac{1}{2}) - \omega''_e(n'' + \tfrac{1}{2}) - \\ & \omega'_e x'(n' + \tfrac{1}{2})^2 + \omega''_e x''(n'' + \tfrac{1}{2})^2 + \\ & [B'_e + B''_e - \alpha'_e(n' + \tfrac{1}{2}) - \alpha''_e(n'' + \tfrac{1}{2})]j + \\ & [B'_e - B''_e - \alpha'_e(n' + \tfrac{1}{2}) + \alpha''_e(n'' + \tfrac{1}{2})]j^2. \end{aligned} \quad (25)$$

These lines, together with those of the transitions  $j - 1 \rightarrow j$  and  $j \rightarrow j$  (if the latter occur) form a band system. The general position of the band system in the spectrum is fixed by the largest term, namely  $\nu_{el}$ . Each band system contains many vibrational bands. In lowest order of approximation these will be linearly arranged with the two sets of spacings  $\omega'_e$  and  $\omega''_e$ . In higher order the linear spacings will be modified by the convergence terms which are proportional to  $\omega'_e x'$  and  $\omega''_e x''$ . Each vibration band is composed of rotation lines the positions of which depend mainly upon the two terms  $(B'_e + B''_e)j$  and  $(B'_e - B''_e)j^2$ . Since  $B_e$  is inversely proportional to the square of the equilibrium internuclear distance, it may have quite different values in the two electronic states. Thus the rotational lines usually show a large convergence in contrast to the situation for the pure vibration-rotation band discussed earlier where the convergence depends upon higher order terms and consequently is small.

## 2.4 Symmetry Properties of Homonuclear Molecules

An interesting modification occurs if the diatomic molecule is homonuclear (as  $H_2$ ,  $N_2$ ,  $O_2$ , etc.). The system now contains two identical particles, namely the two nuclei. Since the nuclei are rigorously identical the Hamilton-

ian and hence the wave equation must be invariant if the particles are interchanged. The situation is the same as that for the helium atom with its two identical electrons (Chapter 1, § 9, in this volume). The wave functions divide into two classes, the symmetrical functions which are unchanged for an interchange of the particles,  $\psi_s(12) = \psi_s(21)$  and the antisymmetric functions  $\psi_a(12) = -\psi_a(21)$ . The Pauli Principle states that for particles with integral spin, including zero, only the symmetric functions occur in nature while for half odd integer spin only the antisymmetric functions occur. The total wave function of the diatomic molecule, to a high order of approximation,\* may be separated into electronic, vibrational, rotational and nuclear spin factors

$$\psi = \psi_{el} \psi_{vib} \psi_{rot} \psi_{sp}. \quad (26)$$

$\psi$  must be either symmetric or antisymmetric depending upon the spin of the nuclei but the individual factors may have any symmetry providing their product has the required symmetry. Obviously the product of two symmetric or of two antisymmetric functions is symmetric while the product of a symmetric and an antisymmetric function is antisymmetric.

The vibrational and rotational wave functions depend upon the coordinates of the nuclei only. Since the two identical nuclei are interchanged by a reflection of the nuclear coordinates at the origin (the center of mass of the molecule), the symmetry property of these functions is given by their parity. The vibrational factor,  $\psi_{vib}$ , always remains unchanged by a reflection at the origin since it depends only on the magnitude of the internuclear distance. The rotational wave functions are the surface harmonics, and since these have even parity for states of even  $j$  and odd parity for states of odd  $j$  (Vol. I, Chapter 3, § 3.1), the rotational factors,  $\psi_{rot}$ , are symmetric functions for states of even  $j$  and antisymmetric functions for states of odd  $j$ . The factor  $(\psi_{el} \psi_{vib} \psi_{rot})$  will therefore be alternately symmetric, for states of even  $j$ , and antisymmetric, for states of odd  $j$ , if the electronic wave function is a symmetric function; while it will be alternately antisymmetric, for even  $j$ , and symmetric, for odd  $j$ , if the electronic wave function is an antisymmetric function.

If the two identical nuclei of the molecule have zero spin (as in  $(O^{16})_2$ ) only the symmetric wave functions can occur in nature. Since the nuclear spin factor of the wave function for such a molecule (namely unity) is clearly symmetric the product of the electronic, vibrational, rotational, and nuclear

\* The symmetry of the wave function is a rigorous property following from the identity of the nuclei. The results to be obtained are therefore not dependent upon the approximate nature of the wave functions used in the argument.

spin factors will be symmetric only for states of even  $j$  in a symmetric electronic state, and for states of odd  $j$  in an antisymmetric electronic state. In such a molecule therefore the states of odd  $j$  in a symmetric electronic state and the states of even  $j$  in an antisymmetric electronic state must be nonexistent. As a result alternate lines in the rotational fine structure will be completely missing in a transition between two electronic states of opposite symmetry. (Transitions  $\Sigma \rightarrow \Sigma$  between electronic states of the same symmetry are forbidden in such a molecule by the selection rule  $\Delta j = \pm 1$ . Transitions involving states with  $\Lambda \neq 0$  will be discussed in more detail below.)

If the two identical nuclei have a spin greater than zero the possible number of nuclear spin configurations always leads to the existence of both symmetric and antisymmetric nuclear spin wave functions. If the nuclei have a spin of  $\frac{1}{2}$  for example, as in  $H_2$ , there are three symmetric and one antisymmetric nuclear spin functions where these have exactly the same form as the electron spin functions for the helium atom (cf. Chapter 1, § 7.7, in this volume). As a result both even and odd  $j$  levels can occur in nature though they occur with different statistical weights. Since the total wave function must be antisymmetric to the interchange of the two identical spin  $\frac{1}{2}$  nuclei, a symmetric factor ( $\psi_{el} \psi_{vib} \psi_{rot}$ ) can combine only with the single antisymmetric nuclear spin function, while an antisymmetric factor ( $\psi_{el} \psi_{vib} \psi_{rot}$ ) can combine with any of the three symmetric nuclear spin functions. The even and odd  $j$  levels therefore form two term systems with statistical weights differing by the ratio 1 to 3, or 3 to 1, depending on the symmetry of the electronic part of the wave function.

Since the components of the electric dipole moment of a homonuclear diatomic molecule are invariant to an interchange of the two identical nuclei, and since the electric dipole moment of the molecule is independent of the orientations of the nuclear spins, transitions can occur only between states for which the factors ( $\psi_{el} \psi_{vib} \psi_{rot}$ ) have the same symmetry. The integrals

$$\int (\psi_{el} \psi_{vib} \psi_{rot})_{initial}^* \mu_k (\psi_{el} \psi_{vib} \psi_{rot})_{final} d\tau$$

which determine the transition probability for dipole radiation cannot change sign if the two identical nuclei are exchanged. A transition from a state with a symmetric factor ( $\psi_{el} \psi_{vib} \psi_{rot}$ ) to a state with an antisymmetric factor ( $\psi_{el} \psi_{vib} \psi_{rot}$ ) could result only from a perturbation coupling the nuclear spins to the other degrees of freedom of the molecule.\* Since such

\* In such a case the separation of the wave function into a nuclear spin factor and a factor involving only the other degrees of freedom would of course be valid only in zeroth order.

perturbations are extremely weak, it may take weeks or months before a molecule in a gas such as  $H_2$  makes a transition from a state of one term system to a state of the other. As a result it is often useful to consider the gas to be a mixture of two independent gases. The modification with the greater statistical weight is called the ortho-modification and that with the smaller statistical weight the para-modification. Since a radiative transition can take place only from one ortho state to another ortho state or from one para state to another para state the rotational fine structure of an electronic transition in a molecule such as  $H_2$  shows a 3 to 1 alternation of intensities.

A similar alternation of intensities is observed in all other homonuclear diatomic molecules; the intensity ratio being a function of the nuclear spin. If the two identical nuclei have a spin  $I$ , each nuclear spin has  $(2I + 1)$  possible orientations in an internal molecular (or an external applied) magnetic field.  $M_I = I, \dots, -I$ . As a result there are  $(2I + 1)^2$  possible spin configurations in the molecule. In  $(2I + 1)$  of these the orientations of the two nuclear spins is exactly the same, that is,  $M_{I_1} = M_{I_2}$ . Such functions are obviously unchanged by an interchange of the two identical nuclei.\* The remaining  $[(2I + 1)^2 - (2I + 1)]$  spin functions can be grouped in pairs such as

$$\psi_{M'}(1)\psi_{M''}(2) \quad \text{and} \quad \psi_{M''}(1)\psi_{M'}(2) \quad (27a)$$

where  $M' \neq M''$  and 1 and 2 identify the two nuclei. However, if a small interaction between the two nuclear spins is taken into account the correct zeroth-order stabilized eigenfunctions are not the above but are given by the linear combinations

$$\frac{1}{\sqrt{2}} [\psi_{M'}(1)\psi_{M''}(2) + \psi_{M''}(1)\psi_{M'}(2)] \quad (27b)$$

and

$$\frac{1}{\sqrt{2}} [\psi_{M'}(1)\psi_{M''}(2) - \psi_{M''}(1)\psi_{M'}(2)]$$

The first is clearly symmetric while the second is antisymmetric to an interchange of nuclei 1 and 2. Of the  $[(2I + 1)^2 - (2I + 1)]$  spin functions with  $M' \neq M''$  one half are therefore symmetric while the other half are

\* In the discussion it has been assumed that the two spins are uncoupled by the magnetic field so that  $M_{I_1}$  and  $M_{I_2}$  are good quantum numbers. Again, since the symmetry property of the wave function is a rigorous property following only from the identity of the two nuclei, the results obtained are independent of the exact coupling scheme.

antisymmetric functions, and the total number of symmetric spin functions is  $(2I + 1) + \frac{1}{2}[(2I + 1)^2 - (2I + 1)] = (I + 1)(2I + 1)$  while the total number of antisymmetric spin functions is  $\frac{1}{2}[(2I + 1)^2 - (2I + 1)] = I(2I + 1)$ . In general therefore the rotational fine structure of the electronic transitions in a homonuclear diatomic molecule shows an  $(I + 1)$  to  $I$  alternation of intensities since the even and odd  $j$  levels have statistical weights which alternate in the ratio  $(I + 1)$  to  $I$ . The experimental measurement of the alternating intensities has proved to be one of the fruitful methods for determining nuclear spins.

Since the statistical weight of a given rotational level  $j$  depends not only on the symmetry of the total wave function but also on the symmetry of the electronic part of the wave function, the latter must be discussed in somewhat more detail. The symmetry property of the electronic wave function with respect to an exchange of identical nuclei is related to its spatial symmetry. In the earlier classification of the electronic states into  $\Sigma, \Pi, \Delta, \dots$  states only the axial symmetry of the molecular force field was used. If the two nuclei of the molecule are identical the force field in which the electrons move has also a center of symmetry. In any diatomic molecule in addition any plane containing the internuclear axis is a plane of symmetry for the molecular force field. As a result the electronic wave functions divide into additional symmetry classes: (a) those which are unchanged when all the electrons are reflected in the centre of symmetry, (i.e., when all the electron coordinates  $x_i, y_i, z_i$  are replaced by their negatives,  $-x_i, -y_i, -z_i$ ); (b) those which change sign under this operation, where this symmetry property is indicated by adding the subscript  $g$  or  $u$ , respectively, to the Greek term symbol; (c) those which are unchanged when all the electrons are reflected in a plane containing the internuclear axis; and (d) those which change sign under this symmetry operation, where this latter symmetry property is indicated by adding the superscript  $+$  or  $-$ , respectively, to the term symbol. The electronic states of a homonuclear diatomic molecule are therefore classified by symbols such as  $\Sigma_g^+, \Sigma_u^+, \Sigma_g^-, \Sigma_u^-$ . The superscripts  $+$  and  $-$  and the subscripts  $g$  and  $u$  refer to symmetry operations performed on the *electrons* only, while the statistical weights of the even and odd  $j$  levels depend on the symmetry operation which interchanges the two identical *nuclei*. However, an interchange of the two identical nuclei can be brought about by the following series of symmetry operations which have the net effect of leaving the electrons invariant: (1) A rotation of the whole molecule (nuclei + electrons) through  $180^\circ$  about an axis normal to the internuclear axis followed by a reflection in a plane normal to this axis of rotation and containing the internuclear axis,



and (2) a subsequent reflection of all the electrons in the centre of symmetry. The rotation of the whole molecule through  $180^\circ$  does not affect the electronic part of the wave function, since  $\psi_{el}$  depends only on the coordinates of the electrons relative to the nuclei, so that symmetry operation (1) can only change the sign of  $\psi_{el}$  for the  $-$  states, while operation (2) changes the sign only for  $u$  states. As a result the electronic part of the wave function will be symmetric to an interchange of the two identical nuclei for states such as  $\Sigma_g^+$  and  $\Sigma_u^-$ , while it will be antisymmetric for states such as  $\Sigma_g^-$  and  $\Sigma_u^+$ .

The above discussion was purposely restricted to the nondegenerate  $\Sigma$  states. In the  $\Pi, \Delta, \dots$  states there is a twofold degeneracy for the non-rotating molecule, but both symmetries occur, since it can be shown that the correct zeroth-order stabilized eigenfunctions must be built up from the two possibilities in such a way that one is  $(+)$  the other  $(-)$ ; however both have the same symmetry with respect to reflection of the electrons in the centre, either  $g$  or  $u$ . As has already been mentioned this degeneracy of the  $(+)$  and  $(-)$  components is removed by the interaction between the rotation and the electronic angular momentum ( $\Lambda$ -type doubling). In each rotational state of a  $\Pi, \Delta, \dots$  state, therefore, one component level has a factor  $(\psi_{el} \psi_{vib} \psi_{rot})$  which is symmetric to an interchange of the two identical nuclei while the other is antisymmetric. If the  $\Lambda$ -type doubling is too small to be experimentally observable no alternation of intensities is observed in a  $\Pi \rightarrow \Pi$  transition, for example, since both ortho and para states contribute to each rotational line

Since the electric dipole moment vector changes sign upon reflection in the origin but is invariant to a reflection in a plane containing the internuclear axis, the selection rules

$$\begin{aligned} g &\leftrightarrow u, & g &\leftrightarrow | \rightarrow g, & u &\leftrightarrow | \rightarrow u \\ \Sigma^+ &\leftrightarrow \Sigma^+, & \Sigma^- &\leftrightarrow \Sigma^-, & \Sigma^+ &\leftrightarrow | \rightarrow \Sigma^- \end{aligned}$$

must be added to the electronic selection rules  $\Delta\Lambda = 0, \pm 1$ .\*

### 3. Polyatomic Molecules

#### 3.1 Vibrational Spectrum

Because of the great complexity of their fine structure the analysis of the electronic spectra of polyatomic molecules remains in an exploratory stage, so that only vibration-rotation spectra will be considered here,

\* The symbol  $\leftrightarrow$  means that the states in question are connected by a radiative transition while the symbol  $\leftrightarrow | \rightarrow$  means that no radiative transition can exist

although the basic principles needed for an understanding of the electronic spectra are the same as those for the diatomic molecule. In most polyatomic molecules the electronic ground state is free of electronic angular momentum, and the ground state wave function remains unchanged under all the symmetry operations of the molecule so that the electronic part of the wave function can play no role in the vibration-rotation spectrum. The diatomic molecule shows that the vibration-rotation Hamiltonian separates in zeroth approximation into pure vibrational and rotational terms. Because of the large difference in the order of magnitude of the vibrational and rotational frequencies, the interactions between vibration and rotation play only a minor role in the case of polyatomic molecules also. The zeroth order pure vibrational and pure rotational terms will therefore be considered first. The effect of the vibration-rotation interactions can be treated by perturbation theory. Although these can often complicate the appearance of the rotational structure of the spectra they can usually be expressed, as in the case of the diatomic molecule, as the higher order terms in a rapidly converging power series in the vibrational and rotational quantum numbers.

In a polyatomic molecule of  $N$  atoms the  $3N$  degrees of freedom describing the motion of the nuclei divide into three sets, namely the three degrees of translation for the entire system, the three degrees of rotation, and  $(3N - 6)$  degrees which describe the mutual vibrations of the nuclei.\* As in the diatomic molecule the extent of the vibrational wave functions is small compared with the internuclear distances. If the  $3N - 6$  vibrational coordinates ( $q_i$ ,  $i = 1, 2, \dots, 3N - 6$ ) are chosen to measure the small displacements of the nuclei from their equilibrium position a development of the potential energy as a power series in the  $q_i$  is justified.† Then

$$V = V_0 + \frac{1}{2} \sum_{i,j=1}^{3N-6} \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 q_i q_j + \frac{1}{3!} \sum_{i,j,k=1}^{3N-6} \left( \frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k} \right)_0 q_i q_j q_k \quad (28)$$

+ ... higher order terms

The constant  $V_0$  can be set equal to zero if the energy is measured from the minimum of the potential function. The terms linear in  $q_i$  are missing because of the equilibrium conditions  $(\partial V / \partial q_i)_0 = 0$ . Terms cubic in the  $q_i$  as well as higher order terms can be neglected to within a good zeroth-order

\* In the case of a linear molecule there are only two degrees of rotational freedom and hence  $(3N - 5)$  degrees of vibration.

† Since the  $q_i$  are to measure the mutual vibrations of the nuclei and not the rotation or translation of the molecule they must be so chosen that an increase in any  $q$  does not produce either a linear or angular momentum of the molecule as a whole.

approximation. The potential energy can therefore be approximated by a homogeneous quadratic function of the  $q_i$ . The kinetic energy must be a homogeneous quadratic function of the time derivatives  $\dot{q}_i$ .

$$T = \frac{1}{2} \sum_{i,j=1}^{3N-6} a_{ij} \dot{q}_i \dot{q}_j. \quad (29)$$

The  $a_{ij}$  are in general functions of the coordinates  $q_i$  which may, however, again be expanded in Taylor series about the equilibrium configuration and in zeroth approximation may be regarded as constants independent of the  $q_i$ .

To within this approximation the problem becomes soluble, both in classical mechanics and in quantum mechanics, by the method of normal coordinates. It is always possible to introduce new coordinates  $Q_i$ , the so-called normal coordinates, which are linear combinations of the  $q_i$  and which transform the kinetic and potential energies into the simple forms,

$$T = \frac{1}{2} \sum_{i=1}^{3N-6} \dot{Q}_i^2 \quad (30a)$$

$$V = \frac{1}{2} \sum_{i=1}^{3N-6} \lambda_i Q_i^2. \quad (30b)$$

As is well-known from classical mechanics the  $\lambda_i$  are the roots of the secular determinant

$$a_{ij}\lambda - \frac{\partial^2 V}{\partial q_i \partial q_j / 0} = 0.$$

The vibrational Hamiltonian when expressed in normal coordinates is clearly

$$H_{\text{vib}} = \sum_{i=1}^{3N-6} H_i \quad (31a)$$

where

$$H_i = \frac{1}{2} P_i^2 + \frac{1}{2} \lambda_i Q_i^2. \quad (31b)$$

The resulting wave equation  $H\psi = E\psi$  separates into  $3N - 6$  equations each describing a simple harmonic oscillator. Thus

$$\psi = \psi_1(Q_1) \psi_2(Q_2) \dots \psi_{3N-6}(Q_{3N-6}) \quad (32)$$

$$E = \sum E_i, \quad \text{and} \quad E_i = (n_i + \frac{1}{2}) h \nu_i, \quad \text{with} \quad 2\pi \nu_i = \sqrt{\lambda_i}.$$

It is not necessary that the  $\lambda_i$  should all be distinct and in fact for molecules with a high degree of symmetry two or even three  $\lambda$ 's coincide. This gives rise to a degeneracy since if  $\lambda_i = \lambda_j$ ,  $E_i$  is identical with  $E_j$ . Together the combined energy term is  $(n_i + 1)h\nu$ , and has a multiplicity or weight easily seen to be  $(n_i + 1)$ .

The selection rules and intensities of the transitions are given by the matrix elements of the electric dipole moment. The components of the electric dipole moment, in general, depend on the displacements of the nuclei in a complicated way, but since the vibrational motions correspond to small oscillations about the equilibrium position the dipole moment components can be expanded in power series in the normal coordinates

$$\mu_k = \mu_k^{(0)} + \sum_{i=1}^{3N-6} \left( \frac{\partial \mu_k}{\partial Q_i} \right)_0 Q_i + \text{higher order terms} \quad (33)$$

where terms quadratic, cubic, and higher order in the normal coordinates can be neglected to a very good zeroth approximation. The components of the permanent dipole moment,  $\mu_x^{(0)}$ ,  $\mu_y^{(0)}$ ,  $\mu_z^{(0)}$  as in the diatomic molecule, give rise to the pure rotational spectrum and have no influence on the vibrational transitions. In zeroth approximation, therefore, the vibrational intensities are governed by integrals of the type

$$\begin{aligned} & \left( \frac{\partial \mu_k}{\partial Q_i} \right)_0 \int \psi_{n_i}^*(Q_1) \psi_{n_i + \Delta n_i}(Q_1) dQ_1 \cdot \\ & \int \psi_{n_2}^*(Q_2) \psi_{n_2 + \Delta n_2}(Q_2) dQ_2 \cdot \dots \int \psi_{n_i}^*(Q_i) Q_i \psi_{n_i + \Delta n_i}(Q_i) dQ_i \cdot \dots \end{aligned} \quad (34)$$

Since these wave functions are just those of simple harmonic oscillators, it is clear that the entire integral will vanish unless  $\Delta n_i = \pm 1$  and  $\Delta n_k = 0$  for  $k \neq i$ . Thus only those vibrational transitions can occur in which only one of the vibrational quantum numbers changes by one unit and provided at least one of the coefficients  $(\partial \mu_x / \partial Q_i)_0$ ,  $(\partial \mu_y / \partial Q_i)_0$ ,  $(\partial \mu_z / \partial Q_i)_0$  is different from zero. The vibrational spectrum predicted by quantum theory is therefore to this approximation identical with the classical spectrum, i.e., the vibrational bands will have the frequencies of the classical fundamentals and they will appear only if the normal vibration in question involves a change in the electric moment.

The higher order vibrational terms which have been neglected so far not only lead to slight modifications in the frequencies and the intensities of the vibrational fundamentals but also lead to the existence of weak

vibrational overtones ( $\Delta n_i = 2, 3, \dots$ ) and combination bands ( $\Delta n_i = +1$ ,  $\Delta n_j = +1$  simultaneously,  $\dots$ ). If the cubic and quartic potential constants in (28) and the higher order terms in (29) are introduced as perturbation terms, a second order perturbation calculation leads to the following expression for the purely vibrational energy

$$E_{n_1 n_2 \dots n_i \dots} = \sum_{i=1}^{3N-6} h\nu_i (n_i + \frac{1}{2}) + \sum_{i,j=1}^{3N-6} X_{ij} (n_i + \frac{1}{2})(n_j + \frac{1}{2}) \quad (35)$$

where the constants  $X_{ij}$ , which give the effect of the anharmonicity and correspond to  $\omega_e x$  for the diatomic molecule, are small compared with the  $h\nu_i$ , so that the energy levels corresponding to a particular normal mode are still nearly equally spaced. The overtones and combination bands become active through the higher order anharmonic constants in two ways. The electrical anharmonicities (higher order terms in the dipole moment expansions, (33)) in combination with the zeroth-order wave functions can lead to transitions such as  $\Delta n_i = 2, \dots$ , while the mechanical anharmonic constants of (28) and (29) give perturbation corrections to the wave functions which in combination with the dominant terms in the dipole moment expansions lead to the same type of transitions. The calculation of the intensities of the weak overtone and combination bands is therefore a complicated higher order problem. The selection rules, however, can be determined from the symmetries of the wave functions alone.

### 3.2 Group Theory Considerations

The methods of group theory form a valuable tool in the study of molecular vibrations, since many polyatomic molecules have a high degree of symmetry, and since the selection rules for the vibrational fundamentals and their overtones can be found solely from the symmetry of the equilibrium configuration of the molecule. In addition, only the molecular symmetry is needed to determine the number and characteristics of the fundamental frequencies as well as their degeneracies, the possibility of the splitting of the overtone levels of degenerate modes, and the possibility of perturbations due to resonance between different vibrational states. Symmetry considerations can also be used to simplify the calculation of the normal frequencies by bringing about a splitting of the  $(3N - 6) \times (3N - 6)$  secular determinant, which fixes the  $\lambda$ 's, into a number of smaller subdeterminants.

The use of symmetry considerations will be illustrated by considering a specific example, the methyl chloride molecule,  $\text{ClCH}_3$ , although the remarks to be made apply generally to any molecular system. In the equilibrium

configuration of this molecule the  $\text{CH}_3$  group has the structure of a regular pyramid with the carbon at the apex, the three equivalent hydrogens forming an equilateral triangle at the base. The Cl atom lies above the C atom on the extension of the symmetry axis of the  $\text{CH}_3$  group. If the molecule is rotated through an angle of  $120^\circ$  about the threefold  $\text{CH}_3$  symmetry axis it assumes an equilibrium configuration indistinguishable from the original one. During the vibrational motions the instantaneous configurations of the molecule may no longer have the threefold symmetry of the methyl group, but if the above symmetry operation is applied to the distorted molecule, the interatomic distances and angles in the resultant new configuration will be exactly the same as those in the original one. The potential and kinetic energies and hence the Hamiltonian are clearly invariant under the symmetry operations of the equilibrium configuration. Besides the threefold rotation, designated by  $C_3$ , the symmetry operations  $C_3^2$ , rotation through an angle of  $240^\circ$  about the threefold axis, and  $\sigma^{(1)}$ ,  $\sigma^{(2)}$ ,  $\sigma^{(3)}$ , reflections in the three HCCl planes, also leave the Hamiltonian of the molecule invariant. These five symmetry operations, together with the identity operation,  $E \equiv C_3^3 \equiv [\sigma^{(i)}]^2$ , form a group of order 6, the axial point group  $C_{3v}$ . The character table for this group is shown in Table II. The symmetry operations divide into three conjugate classes so that there are three irreducible representations or species of which two,  $A_1$  and  $A_2$ , are of dimension 1, and one,  $E$ , of dimension 2.\*

The transformation properties of the normal coordinates of the molecule follow from the invariance of the potential energy to the symmetry operations of the group. If the symmetry operation  $R$  is performed on the molecule, the potential energy in the transformed configuration must be equal to the potential energy in the original configuration

$$2V = \sum_{i=1}^{3N-6} \lambda_i (RQ_i)^2 = \sum_{i=1}^{3N-6} \lambda_i Q_i^2. \quad (36)$$

If  $Q_k$  is a particular nondegenerate normal coordinate, i.e., if there is only one  $\lambda$  with the particular value  $\lambda_k$ , then  $(RQ_k)^2 = Q_k^2$  and consequently  $RQ_k = \pm Q_k$ . The symmetry operation  $R$  acting on  $Q_k$  must change  $Q_k$  either into itself or it can at most change its sign. The transformation properties of the degenerate modes are more complicated. If  $Q_{ja}$  and  $Q_{jb}$  are a pair of normal coordinates belonging to the doubly degenerate mode,

\* The sum of the squares of the dimensions of the irreducible representations must be equal to 6, the order of the group.

$\lambda_{ja} = \lambda_{jb} = \lambda_j$ , the invariance of the potential energy to the symmetry operation  $R$  requires

$$(RQ_{ja})^2 + (RQ_{jb})^2 = Q_{ja}^2 + Q_{jb}^2 \quad (37)$$

so that  $R$  may transform  $Q_{ja}$  and  $Q_{jb}$  into linear combinations of the original  $Q_{ja}$  and  $Q_{jb}$ . In general, for an  $n$ -fold degenerate normal coordinate

$$RQ_{j\alpha} = \sum a_{j\gamma\alpha}(R)Q_{j\gamma} \quad (38)$$

where  $a_{j\gamma\alpha}$  is an orthogonal matrix, and where the summation is over the  $n$  values of  $j$  for which  $\lambda_{j\gamma} = \lambda_{j\alpha}$ . If the operation  $R$  is followed by another symmetry operation  $S$ , then

$$SRQ_{j\alpha} = \sum a_{j\gamma\alpha}(R)SQ_{j\gamma} = \sum \sum a_{j\gamma\alpha}(R)a_{j\delta\gamma}(S)Q_{j\delta}. \quad (39)$$

Since the product of the symmetry operations  $R$  and  $S$  must be one of the symmetry operations of the group, say  $T = SR$ , and since

$$TQ_{j\alpha} = \sum a_{j\delta\alpha}(T)Q_{j\delta} \quad (40)$$

the transformation coefficients must be related by

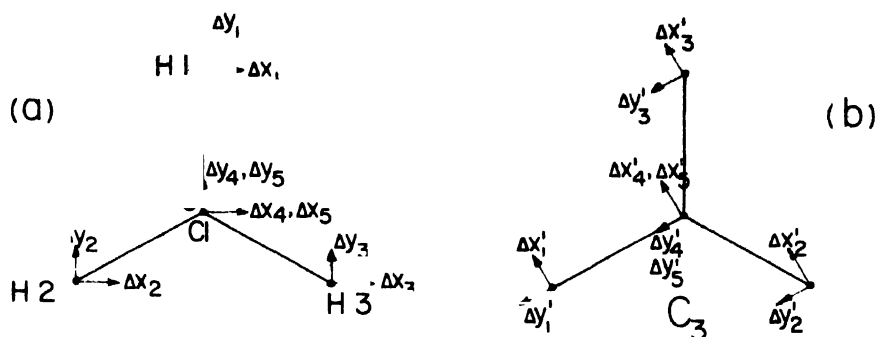
$$a_{j\delta\alpha}(T) = \sum a_{j\delta\gamma}(S)a_{j\gamma\alpha}(R) \quad (41)$$

and thus the matrices  $\mathbf{a}$  form a representation of the group of dimension equal to the degeneracy of the normal mode. The representation which is thus generated by the normal coordinates of a single eigenvalue  $\lambda_j$  must be an irreducible representation. If such a representation were reducible it would be possible to form sets of linear combinations of the original normal coordinates in such a way that all operations of the group would transform one of the normal coordinates of the new sets into linear combinations involving only members of the same set. If this were possible, however, the vibrational frequencies of the new sets could in principle be different, contrary to the original assumption. Such an accidental degeneracy, not required by the symmetry of the molecule, could occur only in very rare cases and would almost certainly be removed by higher order terms in the Hamiltonian. The normal coordinates therefore form bases for the irreducible representations of the group of symmetry operations (of the equilibrium configuration) of the molecule.

The normal coordinates are themselves linear combinations of  $(3N - 6)$  vibrational displacement coordinates,  $q_i$ . If we choose the  $q_i$  in such a way that they transform under the molecular symmetry operations like the base vectors of the irreducible representations, then cross-product terms of the form  $a_{ij}\dot{q}_i\dot{q}_j$  and  $(\partial^2 V / \partial q_i \partial q_j)_0 q_i q_j$ , where  $q_i$  and  $q_j$  belong to *different* irreducible representations, must be missing from the expressions for the potential and kinetic energy. The choice of such symmetry coordinates therefore leads to a factoring of the vibrational problem into  $k$  completely independent problems, where  $k$  is equal to the number of irreducible representations which contain at least one normal vibrational mode. To determine the number of vibrational frequencies belonging to each particular irreducible representation it is necessary only to form a reducible representation based upon any arbitrary set of  $3N - 6$  vibrational coordinates and break this reducible representation down into its irreducible components. The number of distinct vibrational frequencies is then equal to the number of irreducible representations obtained. The degeneracy of a given frequency is equal to the dimension of the corresponding irreducible representation, and the normal coordinates that belong to this frequency transform under the molecular symmetry operations according to the matrices of the corresponding irreducible representation. It is usually simpler to form a reducible representation based not on  $(3N - 6)$  vibrational coordinates but rather on all the  $3N$  coordinates describing the motion of the nuclei, including the 3 translational and 3 rotational degrees of freedom. This follows since it is relatively easy to determine the character of the representation generated by the  $3N$  cartesian displacement coordinates,  $\Delta x_1, \Delta y_1, \Delta z_1, \dots, \Delta x_N, \Delta y_N, \Delta z_N$ , where the vector with components  $\Delta x_i, \Delta y_i, \Delta z_i$ , attached to the  $i$ th nucleus, measures the displacement of this nucleus from its equilibrium position. The reduction of this representation,  $\Gamma_{3N}$ , will give not only the number of vibrational frequencies in each irreducible representation but will count also the number of translational and rotational motions. Since the translational degrees of freedom transform in the same way as the components of any vector, say  $(x, y, z)$ , while the rotational degrees of freedom transform like a pseudovector,  $(yZ - zY), (zX - xZ), (xY - yX)$ , where  $(x, y, z)$  and  $(X, Y, Z)$  are any vectors, it is easy to reduce the representations based on these quantities into their irreducible components and subtract these from the representation  $\Gamma_{3N}$  to obtain the number of true vibrational frequencies in each irreducible representation.

The method will be illustrated for  $\text{ClCH}_3$ . The cartesian displacement coordinates of  $\text{ClCH}_3$  are shown in Fig. 3 which also shows the effect of the symmetry operation  $C_3$  on the displacement coordinates. The character of





	$\Delta x_1$	$\Delta y_1$	$\Delta z_1$	$\Delta x_2$	$\Delta y_2$	$\Delta z_2$	$\Delta x_3$	$\Delta y_3$	$\Delta z_3$	$\Delta x_4$	$\Delta y_4$	$\Delta z_4$	$\Delta x_5$	$\Delta y_5$	$\Delta z_5$
$\Delta x'_1$	0	0	0	$\cos \frac{2\pi}{3}$	$\sin \frac{2\pi}{3}$	0	0	0	0	0	0	0	0	0	0
$\Delta y'_1$	0	0	0	$-\sin \frac{2\pi}{3}$	$\cos \frac{2\pi}{3}$	0	0	0	0	0	0	0	0	0	0
$\Delta z'_1$	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
$\Delta x'_2$	0	0	0	0	0	0	$\cos \frac{2\pi}{3}$	$\sin \frac{2\pi}{3}$	0	0	0	0	0	0	0
$\Delta y'_2$	0	0	0	0	0	0	$-\sin \frac{2\pi}{3}$	$\cos \frac{2\pi}{3}$	0	0	0	0	0	0	0
$\Delta z'_2$	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0
$\Delta x'_3$	$\cos \frac{2\pi}{3}$	$\sin \frac{2\pi}{3}$	0	0	0	0	0	0	0	0	0	0	0	0	0
$\Delta y'_3$	$\sin \frac{2\pi}{3}$	$\cos \frac{2\pi}{3}$	0	0	0	0	0	0	0	0	0	0	0	0	0
$\Delta z'_3$	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
$\Delta x'_4$	0	0	0	0	0	0	0	0	0	$\cos \frac{2\pi}{3}$	$\sin \frac{2\pi}{3}$	0	0	0	0
$\Delta y'_4$	0	0	0	0	0	0	0	0	0	$-\sin \frac{2\pi}{3}$	$\cos \frac{2\pi}{3}$	0	0	0	0
$\Delta z'_4$	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0
$\Delta x'_5$	0	0	0	0	0	0	0	0	0	0	0	0	$\cos \frac{2\pi}{3}$	$\sin \frac{2\pi}{3}$	0
$\Delta y'_5$	0	0	0	0	0	0	0	0	0	0	0	0	$-\sin \frac{2\pi}{3}$	$\cos \frac{2\pi}{3}$	0
$\Delta z'_5$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1

FIG. 3. (a) Top view of  $\text{ClCH}_3$  showing the Cartesian displacement coordinates. The hydrogens are labelled atoms 1, 2, and 3, the carbon atom 4, the Cl atom 5. The displacements  $\Delta z$  are not indicated on the figure. (b) Behavior of the displacement coordinates under the transformation  $C_3$ . The shifted atoms ( $1 \rightarrow 2$ ,  $2 \rightarrow 3$ ,  $3 \rightarrow 1$ ) give no contribution to the trace of the transformation matrix:

$$\chi_{3N}(C_3) = 2 [1 + 2 \cos (2\pi/3)] = 0.$$

this transformation of the displacement coordinates, i.e., the trace of the transformation matrix,  $\Gamma_{3N}(C_3)$ , is seen to be  $\chi_{3N}(C_3) = 2[1 + 2 \cos(2\pi/3)]$ . The hydrogen atoms 1, 2, 3 which are shifted to new equilibrium positions by the symmetry operation  $C_3$  clearly can not contribute to the character  $\chi_{3N}(C_3)$ . To find the character of  $\Gamma_{3N}$  for a symmetry operation  $R$  only those atoms must be considered whose equilibrium positions are not altered by  $R$ . Under the symmetry operation  $C_3$  each atom situated on the threefold axis contributes a factor  $1 + 2 \cos 2\pi/3$  to  $\chi_{3N}(C_3)$ . In general the character of the representation  $\Gamma_{3N}$  for a symmetry operation  $C_n^k$ , rotation through an angle of  $2\pi k/n$  radians about any  $n$ -fold symmetry axis, is given by  $U[1 + 2 \cos(2\pi k/n)]$ , where  $U$  is equal to the number of atoms whose equilibrium position is left invariant by this operation. Under reflection in one of the ClCH symmetry planes,  $\sigma$ , the equilibrium positions of three of the atoms in ClCH<sub>3</sub> are left invariant. Under reflection in the plane containing H atom 1, for example,  $\Delta y_i \rightarrow +\Delta y_i$ ,  $\Delta z_i \rightarrow +\Delta z_i$ , while  $\Delta x_i \rightarrow -\Delta x_i$  for the invariant atoms  $i = 1, 4$ , and 5 so that  $\chi_{3N}(\sigma) = 3(2 - 1)$ . In the general case of a rotation-reflection operation,  $S_n^k$ , rotation through an angle  $2\pi k/n$  about an  $n$ -fold rotation-reflection axis, followed by a reflection in a plane normal to this axis, the character of  $\Gamma_{3N}$  is given by  $U[-1 + 2 \cos(2\pi k/n)]$ . The pure reflection operation is a special case with  $n = 1$ ,  $k = 1$ . Another special case is that of reflection in a center of inversion,  $i$ , which is identical with the symmetry operation  $S_2$ . Finally, the identity operation,  $E$ , leaves all  $3N$  displacement coordinates unchanged so that  $\chi_{3N}(E) = 3N$ . The characters for the representation  $\Gamma_{3N}$  are shown in Table II for ClCH<sub>3</sub>. Breaking this reducible representation down into its irreducible components, one obtains by the usual methods (see Chapter 2, § 1.7 and § 3.2, in this volume)

$$\Gamma_{3N} = 4A_1 + A_2 + 5E. \quad (42)$$

In order to obtain the number of vibrational frequencies in each irreducible representation, the translations and rotations must still be subtracted from  $\Gamma_{3N}$ . The transformation matrices of the three translational degrees of freedom,  $t$ , or for that matter the components of any vector  $(x, y, z)$ , must be the same as those for the displacement vector  $\Delta x_4, \Delta y_4, \Delta z_4$  of Fig. 3, for example. The characters of the representation,  $\Gamma_t$ , are therefore given by

$$\begin{aligned} \chi_t(E) &= 3, \\ \chi_t(C_n^k) &= [1 + 2 \cos(2\pi k/n)], \\ \chi_t(S_n^k) &= [-1 + 2 \cos(2\pi k/n)]. \end{aligned} \quad (43)$$

Similarly, from the transformation properties of an arbitrary pseudovector

such as  $(yZ - zY)$ ,  $(zX - xZ)$ ,  $(xY - yX)$  it can be seen that the characters of the representation based on the three rotational degrees of freedom,  $r$ , are given by

$$\begin{aligned}\chi_r(E) &= 3, \\ \chi_r(C_n^k) &= [2 \cos(2\pi k/n) + 1], \\ \chi_r(S_n^k) &= [-2 \cos(2\pi k/n) + 1].\end{aligned}\quad (44)$$

The values for the point group  $C_{3v}$  are shown in Table II. The reduction into irreducible representations yields

$$\Gamma_t = A_1 + E \quad \text{and} \quad \Gamma_r = A_2 + E.$$

Table II also shows explicitly the transformation properties of the various components of the vector and pseudovector representations. Clearly,  $z$ , the vector component in the direction of the threefold axis is unchanged by all the symmetry operations and belongs to the totally symmetric irreducible representation  $A_1$ , while  $x, y$  form base vectors for the degenerate representation  $E$ .

TABLE II  
CHARACTER TABLE FOR THE POINT GROUP  $C_{3v}$

$C_{3v}$	$E$	$2C_3$	$3\sigma$	
$A_1$	+1	+1	+1	$z$
$A_2$	+1	+1	-1	$xY - yX$
$E$	+2	-1	0	$x, y$ ( $yZ - zY$ ), ( $zX - xZ$ )
$\Gamma_{3N}(\text{ClCH}_3)$	+15	0	+3	
$\Gamma_{3N}(\text{NH}_3)$	+12	0	+2	
$\Gamma_{3N}(\text{NCCH}_3)$	+18	0	+4	
$\Gamma_t$	+3	0	+1	
$\Gamma_r$	+3	0	-1	
$E^{(4)} \times E^{(6)}$	+4	+1	0	
$[E^{(4)}]^2$	+3	0	+1	
Nuclear spin				
states $\Gamma_I(I = \frac{1}{2})$	8	2	4	
(see § 3.7) $\Gamma_I$	$(2I + 1)^3$	$(2I + 1)$	$(2I + 1)^2$	

The  $(3N - 6)$  dimensional representation which has the vibrational coordinates as its basis is obtained by subtracting  $\Gamma_t$  and  $\Gamma_r$  from  $\Gamma_{3N}$ , giving  $\Gamma_{\text{vib}} = 3A_1 + 3E$  for  $\text{ClCH}_3$ . The methyl chloride molecule therefore

has 6 distinct vibrational frequencies, where the normal coordinates associated with 3 of the frequencies, commonly designated  $\nu_1, \nu_2, \nu_3$ , transform according to the totally symmetric representation  $A_1$  while the normal coordinates associated with the other three frequencies ( $\nu_4, \nu_5, \nu_6$ ) occur in doubly degenerate pairs of symmetry  $E$ .

The symmetries of the wave functions follow from the symmetries of the normal coordinates. The zeroth-order\* wave functions are the harmonic oscillator wave functions

$$\psi_{n_1, n_2, \dots, n_6}^{(0)} = \exp\left(-\frac{1}{2} \sum_i \alpha_i Q_i^2\right) \prod_{i=1}^{3N-6} N_{n_i} H_{n_i}(\sqrt{\alpha_i} Q_i), \quad (45)$$

$$\alpha_i = \sqrt{\lambda_i}/\hbar$$

$H_{n_i}$  being Hermite polynomials of degree  $n_i$ . The sum in the exponential is invariant under all the operations of the molecular symmetry group since it contains terms such as  $\sqrt{\lambda_k} Q_k^2$  for the nondegenerate modes, and  $\sqrt{\lambda_i}(Q_{ia}^2 + Q_{ib}^2)$  for the doubly degenerate modes, and these terms are respectively proportional to the corresponding invariant factors of the potential energy. The ground state wave function therefore transforms according to the totally symmetric representation in every molecule, while the excited state wave functions belong to the same representation as the product of the Hermite polynomials. The wave functions for the fundamental vibrational states,  $n_i = 1$ , all other  $n_j = 0$ , therefore transform like the normal coordinates,  $Q_i$  (since the Hermite polynomial with  $n_i = 1$  is proportional to  $Q_i$ ). The wave functions of the pure overtone states of a nondegenerate frequency  $\nu_i$  transform like even and odd functions of  $Q_i$ , for  $n_i$  even and odd respectively, and therefore belong to the totally symmetric representation for  $n_i$  even and to the representation of  $Q_i$  for  $n_i$  odd. Overtone and combination states involving degenerate normal coordinates are more complicated and will be discussed later.

A transition from a vibrational state  $A$  ( $n_1^A, n_2^A, \dots, n_i^A, \dots$ ) to a state  $B$  ( $n_1^B, n_2^B, \dots, n_i^B, \dots$ ) can occur only if the matrix elements of the dipole moment

$$\psi_A^* \mu_R \psi_B \neq 0 \quad (46)$$

\* Symmetry arguments based on zeroth-order wave functions are of course rigorous since the transformation properties of the wave functions are independent of the order of approximation.

where  $\mu_k$ , ( $k = x, y, z$ ), belongs to the vector representation,  $\Gamma_i$ . The integrals can differ from zero only if the integrands are invariant under all the symmetry operations of the molecular group. Since the integrands belong to the direct product of the representations of  $\psi_A$ ,  $\mu$  and  $\psi_B$ ,  $\Gamma_A \times \Gamma_i \times \Gamma_B$ , the transition  $A \rightarrow B$  can be allowed only if the direct product  $\Gamma_A \times \Gamma_i \times \Gamma_B$  contains the totally symmetric irreducible representation. If the initial state  $A$  is the ground state, as is the case for most absorption spectra taken at room temperature, and since  $\Gamma_A$  is totally symmetric, a transition to the state  $B$  can take place only if the representation  $B$  contains one of the irreducible components of the vector representation. In particular, the fundamental frequency  $\nu_i$  is observed only if the representation of  $Q_i$  is one of the irreducible components of  $\Gamma_i$ .

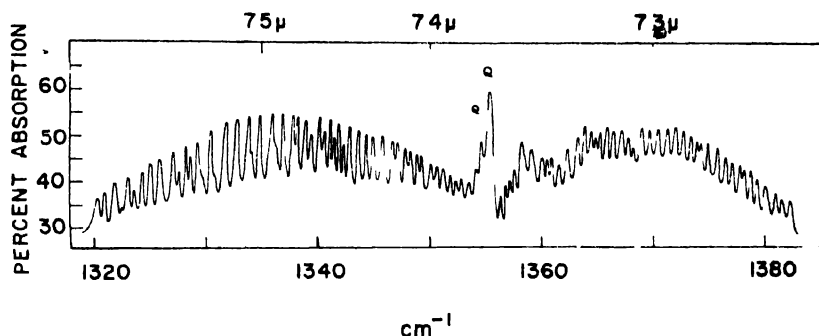


FIG. 4. The parallel band  $\nu_2$  of methyl chloride,  $\text{CH}_3\text{Cl}$ , (after Nielsen and Nielsen<sup>9</sup>). Some of the lines in the  $R$  and  $P$  branch appear double because the  $\text{CH}_3\text{Cl}^{37}$  isotope band which overlaps the  $\text{CH}_3\text{Cl}^{35}$  isotope band is intense enough to be observed. The two bands are nearly coincident. The  $Q$  branches of the two isotopic species are apparently separated by no more than  $1 \text{ cm}^{-1}$ .

In  $\text{ClCH}_3$  therefore all vibrational fundamentals are observed since three of the frequencies,  $(\nu_1, \nu_2, \nu_3)$ , belong to  $A_1$ , the representation of  $\mu_x$ , while the wave functions of the 3 doubly degenerate fundamental states  $(\nu_4, \nu_5, \nu_6)$  transform according to the representation,  $E$ , of  $\mu_x, \mu_y$ . The 3 fundamentals  $A_1$  are produced by a dipole moment change parallel to the molecular symmetry axis, while the 3 fundamentals  $E$  become active through a change of dipole moment perpendicular to the symmetry axis. It will be seen later that the two types of frequencies have different rotational fine structures and hence quite different appearance. The  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  fundamentals give rise to what are called parallel type bands and in  $\text{CH}_3\text{Cl}$  are observed at 2966, 1355, and  $732 \text{ cm}^{-1}$ .<sup>8</sup> The high frequency band is actually split into two bands, a strong band at 2966 and a weaker one at

2879 by the phenomenon of Fermi resonance, consideration of which is being omitted. Strictly speaking  $\nu_1$  lies between these two values but nearer the strong band at  $2966\text{ cm}^{-1}$ . Figure 4 shows  $\nu_2$  as observed by Nielsen and Nielsen.<sup>9</sup> The fundamentals  $\nu_4$ ,  $\nu_5$  and  $\nu_6$  which in  $\text{CH}_3\text{Cl}$  lie at 3042, 1455, and  $1015\text{ cm}^{-1}$  belong to the class of perpendicular bands.  $\nu_6$  as observed by Bennett and Meyer<sup>10</sup> is shown in Fig 5, which also shows the central portion of the spectrum as observed by Burke<sup>18</sup> under higher resolving power.

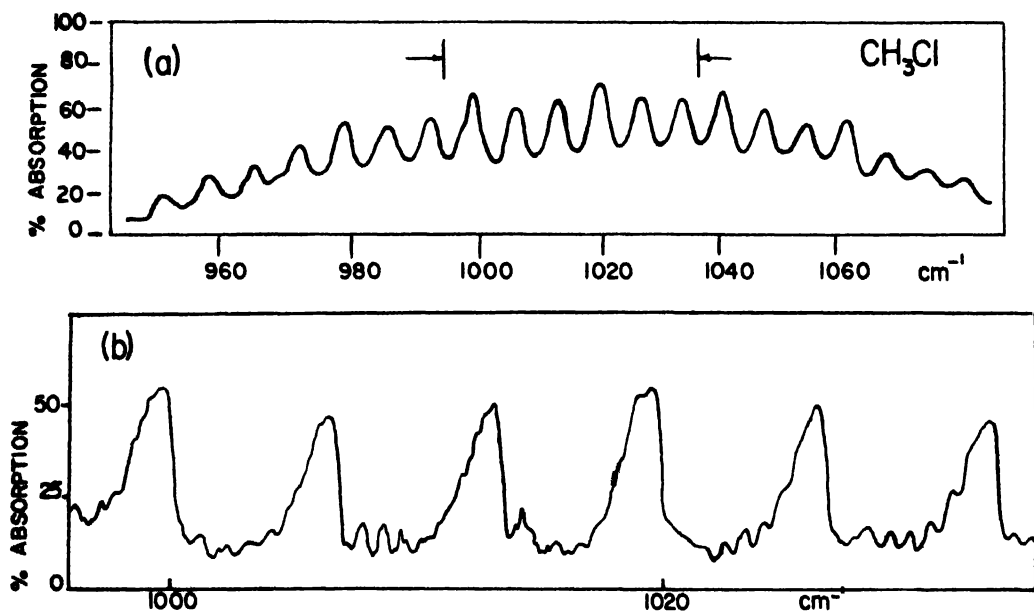


FIG. 5. The perpendicular band  $\nu_6$  of methyl chloride,  $\text{CH}_3\text{Cl}$  (a) Gross structure of the band (Bennett and Meyer<sup>10</sup>) (b) Central portion of the band ( $\rightarrow$  |  $\leftarrow$  of (a)) under higher resolution (Burke<sup>18</sup>)

Overtone and combination bands may also be treated through symmetry considerations. The simplest of these are the overtones and combinations involving only  $\nu_1$ ,  $\nu_2$  and  $\nu_3$ . Since these excited states are all of species  $A_1$  the resulting bands are single and of the parallel type.

The strongest combination bands usually arise through transitions from the ground state to excited states of the type,  $n_i = 1$ ,  $n_j = 1$ , with  $\nu_i \neq \nu_j$ . The wave functions of such a state transform as the direct product of the two different sets of normal coordinates, that is, as  $\Gamma(Q_i) \times \Gamma(Q_j)$ , where the character of the representation of the direct product is equal to the product of the characters of the two representations. If  $\nu_i$  belongs to the species  $A_1$  and  $\nu_j$  to  $E$  the situation is very simple since  $A_1 \times E = E$ . This combination band is therefore single and of the perpendicular type. As a

more complex example consider the combination band  $\nu_4 + \nu_5$  in  $\text{ClCH}_3$ ; a combination involving two different doubly degenerate frequencies. The characters of the direct product  $E^{(4)} \times E^{(5)}$  are shown in Table II. By breaking this direct product into its irreducible representations, one gets

$$E^{(4)} \times E^{(5)} = A_1 + A_2 + E. \quad (47)$$

The fourfold degenerate state,  $n_4 = 1$ ,  $n_5 = 1$ , therefore consists of three substates, and if the higher order vibrational perturbations are taken into account the fourfold zeroth order degeneracy is removed. The state can split into only 3 levels, however, two whose wave functions transform according to the one-dimensional irreducible representations  $A_1$  and  $A_2$ , while the third is a doubly degenerate level whose wave functions transform according to the symmetry  $E$ . No perturbation having the symmetry of the molecule can give rise to a splitting of the  $E$  level. Since transitions from the ground state ( $A_1$ ) can take place only to states  $A_1$  and  $E$ , but *not* to states  $A_2$ , the combination band  $\nu_4 + \nu_5$  must consist of only two vibrational bands, a parallel band and a nearby perpendicular band. The amount of the splitting depends on the strength of the anharmonic forces. However, the form of the correct zeroth-order wave functions is given by symmetry alone and follows from the reduction of the basis functions for the direct product  $E^{(4)} \times E^{(5)}$ . If the doubly degenerate normal coordinates associated with  $\nu_4$  and  $\nu_5$  are called  $Q_{4a}$ ,  $Q_{4b}$ , and  $Q_{5a}$ ,  $Q_{5b}$  respectively, the reduction of the basis formed from their direct product gives the wave functions of the correct symmetry\*

$$\begin{aligned} \psi(A_1) &= N(Q_{4a}Q_{5a} + Q_{4b}Q_{5b}) \exp\left(-\frac{1}{2} \sum_i \alpha_i Q_i^2\right), \\ \psi(A_2) &= N(Q_{4a}Q_{5b} - Q_{4b}Q_{5a}) \exp\left(-\frac{1}{2} \sum_i \alpha_i Q_i^2\right), \\ \psi(E)_a &= N(Q_{4a}Q_{5b} + Q_{4b}Q_{5a}) \exp\left(-\frac{1}{2} \sum_i \alpha_i Q_i^2\right), \\ \psi(E)_b &= N(Q_{4a}Q_{5a} - Q_{4b}Q_{5b}) \exp\left(-\frac{1}{2} \sum_i \alpha_i Q_i^2\right). \end{aligned} \quad (48)$$

The determination of the number and type of active vibrational bands for the pure overtones of the doubly degenerate fundamentals is somewhat

\* To accomplish the reduction the matrices of the irreducible representations must be known. The characters alone are not enough. (See Chapter 2, § 1.7 and § 3.2, in this volume.)

more complicated. The first overtone level of a doubly degenerate frequency, say  $\nu_4$ ,  $n_4 = 2$  has only a threefold zeroth-order degeneracy, [ $g_n = (n + 1)$  for the doubly degenerate modes]. Replacing  $Q_{5a}$ ,  $Q_{5b}$  by  $Q_{4a}$ ,  $Q_{4b}$  in the wave functions of (48) for the combination level  $\nu_4 + \nu_5$ , we note that the wave function of symmetry  $A_2$  becomes identically equal to zero, and we would therefore expect that the overtone state,  $n_4 = 2$ , is made up of levels of symmetry  $A_1$  and  $E$  only. This follows rigorously from the character of the reducible representation based on the three zeroth-order wave functions for the overtone state, namely the three harmonic oscillator functions with  $n_{4a} = 2$ ,  $n_{4b} = 0$ ,  $n_{4a} = 0$ ,  $n_{4b} = 2$ , and  $n_{4a} = 1$ ,  $n_{4b} = 1$ . These basis wave functions have the transformation properties of the 3 products  $Q_{4a}^2$ ,  $Q_{4b}^2$ , and  $Q_{4a}Q_{4b}$ , the highest power terms contributed by the Hermite polynomials. Since the characters of the representation are independent of the choice of coordinate system it is convenient for purposes of determining the characters to choose a set of normal coordinates  $Q_{4a}$  and  $Q_{4b}$  for each symmetry operation  $R$  such that the transformation matrix is diagonal for this particular symmetry operation. This can always be done though it will require a different choice of coordinate system for each  $R$  and may lead to complex transformation matrices. With such a choice

$$R \begin{vmatrix} Q_{4a} \\ Q_{4b} \end{vmatrix} = \begin{vmatrix} a_1 & 0 \\ 0 & a_2 \end{vmatrix} \begin{vmatrix} Q_{4a} \\ Q_{4b} \end{vmatrix} \quad \text{and} \quad R^2 \begin{vmatrix} Q_{4a} \\ Q_{4b} \end{vmatrix} = \begin{vmatrix} a_1^2 & 0 \\ 0 & a_2^2 \end{vmatrix} \begin{vmatrix} Q_{4a} \\ Q_{4b} \end{vmatrix} \quad (49)$$

so that

$$\chi_{n_4}(R) = a_1 + a_2 \quad \text{while} \quad \chi_{n_4}(R^2) = a_1^2 + a_2^2$$

where  $n_4 = 1$ . The character for the reducible representation of the overtone state  $n_4 = 2$ , follows since

$$R \begin{vmatrix} Q_{4a}^2 \\ Q_{4b}^2 \\ Q_{4a}Q_{4b} \end{vmatrix} = \begin{vmatrix} a_1^2 & 0 & 0 \\ 0 & a_2^2 & 0 \\ 0 & 0 & a_1a_2 \end{vmatrix} \begin{vmatrix} Q_{4a}^2 \\ Q_{4b}^2 \\ Q_{4a}Q_{4b} \end{vmatrix} \quad (50)$$

so that

$$\chi_{n_4=2}(R) = a_1^2 + a_2^2 + a_1a_2 = \frac{1}{2}[(a_1 + a_2)^2 + a_1^2 + a_2^2],$$

and the character can also be written

$$\chi_2(R) = \frac{1}{2}\{\chi_1(R)^2 + \chi_1(R^2)\} \quad (51)$$

For the overtone state  $n_4 = 2$  of  $\text{ClCH}_3$  it has the values shown in Table II for the various symmetry operations and the reduction of the representation does give

$$(E^{(4)})^2 = A_1 + E. \quad (52)$$



A pure first overtone of a doubly degenerate frequency in  $\text{ClCH}_3$  therefore gives rise to a parallel band and a nearly superimposed perpendicular band. The actual separation between these bands will depend upon the magnitude of the anharmonic potential.

Expressions for the characters of the higher overtones of doubly degenerate frequencies as well as the characters for triply degenerate frequencies, which occur in more highly symmetrical molecules such as  $\text{CH}_4$ , are given by Tisza.<sup>11</sup>

The ammonia molecule,  $\text{NH}_3$ , and methyl cyanide,  $\text{NCCH}_3$ , are other examples of molecules of symmetry  $C_{3v}$ . The characters for the representations  $\Gamma_{3N}$  for these molecules are also shown in Table II. For  $\text{NH}_3$  the reduction gives

$$\Gamma_{3N} = 3A_1 + A_2 + 4E \quad \text{and} \quad \Gamma_{\text{vib}} = 2A_1 + 2E.$$

For  $\text{NCCH}_3$  it is

$$\Gamma_{3N} = 5A_1 + A_2 + 6E \quad \text{and} \quad \Gamma_{\text{vib}} = 4A_1 + 4E.$$

In both molecules therefore all vibrational fundamentals are active.

As a further example it will be shown that methane,  $\text{CH}_4$ , because of its high degree of symmetry possesses only four distinct vibrational fundamentals although the molecule has nine degrees of vibrational freedom. In its equilibrium configuration the molecule has the structure of a regular tetrahedron with the hydrogens located at the four corners and the carbon nucleus in the center. It therefore belongs to the point group  $T_d$ . The 24 symmetry operations include, besides the identity operation  $E$ , the rotations about the four 3-fold axes,  $C_3$ , defined by the four CH bonds, reflections in the six different HCH planes,  $\sigma_d$ , 2-fold rotations,  $C_2$ , about the three mutually perpendicular axes which bisect opposite H-H lines, and 4-fold rotation-reflections,  $S_4$ , about these same axes. The character table for this point group is shown in Table III. The symmetry operations divide into five conjugate classes. Of the five irreducible representations (or species) two  $A_1$  and  $A_2$ , have dimension 1; and one,  $E$ , has dimension 2; while the remaining two,  $F_1$  and  $F_2$ , have dimension 3. The characters for the representations  $\Gamma_{3N}$ ,  $\Gamma_r$ ,  $\Gamma_v$  can be computed from the general formulas developed in this section, and they are listed in Table III. Under one of the 4-fold rotation-reflection operations, for example, only the central carbon nucleus remains invariant so that the character of  $\Gamma_{3N}$  for this class of symmetry operation, namely  $U[-1 + 2 \cos(2\pi k/n)]$ , has the value of  $-1$  since  $U = 1$ ,  $n = 4$ ,  $k = 1$ , or 3. The reduction of  $\Gamma_{3N}$  by the usual methods gives

$$\Gamma_{3N} = A_1 + E + F_1 + 3F_2.$$

From the character table it can also be seen that the irreducible representations  $F_1$  and  $F_2$  are the pseudovector and vector representations, respectively,  $\Gamma_r = F_1$ ,  $\Gamma_t = F_2$ . Subtracting the contributions of the rotational and vibrational degrees of freedom one therefore gets

$$\Gamma_{\text{vib}} = A_1 + E + 2F_2.$$

TABLE III  
CHARACTER TABLE FOR THE POINT GROUP  $T_d$

$T_d$	$E$	$8C_3$	$6C_2$	$6S_4$	$3C_2$	
$A_1$	+1	+1	+1	+1	+1	
$A_2$	+1	+1	-1	-1	+1	
$E$	+2	-1	0	0	+2	
$F_1$	+3	0	-1	+1	-1	$(Yz - Zy), (Zx - Xz), (Xy - Yx)$
$F_2$	+3	0	+1	-1	-1	$x, y, z$
$\Gamma_{3N}$	15	0	+3	-1	-1	
$\Gamma_t$	+3	0	+1	-1	-1	
$\Gamma_r$	+3	0	-1	+1	-1	
$E \times F_2$	+6	0	0	0	-2	

The molecule has only four distinct vibrational fundamentals, and since the three components of the electric dipole moment transform according to the representation  $F_2$  only the two triply degenerate fundamentals which belong to the irreducible representation  $F_2$  can be observed in the infrared spectrum. The nondegenerate frequency of species  $A_1$  and the doubly degenerate frequency of species  $E$  can be observed only in combination with one of the triply degenerate frequencies of species  $F_2$ . (The direct products  $A_1 \times F_2 = F_2$  and  $E \times F_2 = F_1 + F_2$  both contain the active irreducible representation  $F_2$ .)

### 3.3 Inversion Spectrum of Ammonia

Many polyatomic molecules have potential functions with more than one identical minimum, i.e., such molecules have more than one possible equilibrium configuration. In all nonplanar molecules, for example, the equilibrium configuration of the nuclei is not unique, since a nonplanar molecule can always be turned inside out to transform the nuclear framework into a mirror image of the original one. One possible way of reaching this second configura-

tion from the first is through the inversion of each nucleus in the centre of mass of the molecule. In most cases large forces prevent the molecule from turning itself inside out, that is to say, the two identical potential minima are separated by a large potential barrier. According to classical physics, therefore, the molecule should be trapped in either one or the other of the two possible equilibrium configurations with the nuclei oscillating about this particular equilibrium configuration in their vibrational motions. The molecule would have to absorb an energy many times its vibrational energy to be lifted over the potential hump from one equilibrium configuration to the other. Actually, however, the nuclei need not climb the potential hill to reach the alternate potential minimum, but may penetrate the barrier through the quantum mechanical tunnel effect. Since the two potential minima are identical in height and shape, the states of the molecule will be doubly degenerate if the barrier can be considered infinite — a good approximation for most nonplanar molecules. If the barrier is finite, however, this degeneracy is removed through the tunnel effect which therefore leads to a doubling of all the energy levels of the molecule. Ammonia,  $\text{NH}_3$ , is one of the few nonplanar molecules in which this inversion doubling is large enough to lead to observable splittings in its spectrum.

There are other types of classically forbidden motions in polyatomic molecules for which the quantum mechanical tunnel effect becomes important. An example is the hindered rotation of one part of a molecule with respect to the remainder. The methyl alcohol molecule,  $\text{CH}_3\text{OH}$ , in which the OH bar is inclined at an angle of  $106^\circ$  to the  $\text{CH}_3$  symmetry axis clearly has three identical potential minima corresponding to the three possible equilibrium configurations of the OH bar with respect to the  $\text{CH}_3$  pyramid. The OH bond is not free to rotate about the symmetry axis of the  $\text{CH}_3$  group; but even though the three positions of minimum potential energy are separated by the hills of a hindering potential, the OH unit may penetrate these barriers and tunnel from one equilibrium position to the next. This tunnelling removes the inherent threefold degeneracy of the rotational states and in general splits each level into three. Such hindered rotation splittings have been observed in the microwave spectra of a large number of molecules.<sup>12</sup>  $\text{NH}_3$ , however, provides the simplest and the most extensively studied example of a molecule whose spectrum is complicated by the quantum mechanical tunnel effect.

In its equilibrium configuration  $\text{NH}_3$  forms a symmetrical pyramid of  $\text{C}_{3v}$  symmetry with the N atom at the apex of an equilateral  $\text{H}_3$  triangle (Fig. 6). If the nitrogen can penetrate the  $\text{H}_3$  plane in its motion along the symmetry axis of the pyramid the molecule turns itself inside out. The new

equilibrium configuration in which the N atom lies on the other side of the  $H_3$  plane is not identical with the old configuration as may be seen by numbering the hydrogen atoms. Even though the N spends most of its time

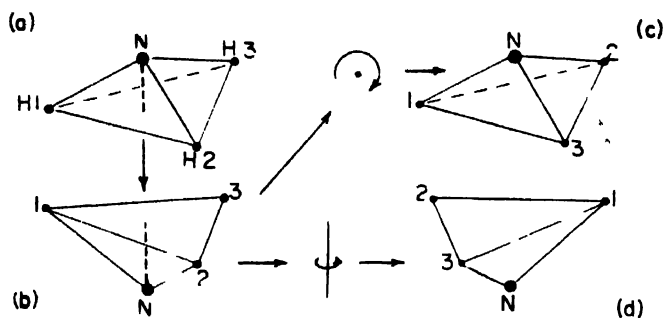


FIG. 6. Inversion of  $NH_3$  (a) Original equilibrium configuration (N atom at the apex of a symmetrical pyramid) (b) New equilibrium configuration after the N atom has penetrated the  $H_3$  plane to turn the molecule inside out (c)  $NH_3$  in its new equilibrium configuration after a rotation Configurations (a) and (c) are distinguishable if the H atoms are given numbers (c) cannot be obtained from (a) solely by a rotation of the whole molecule (d)  $NH_3$  in its new equilibrium configuration after a rotation about the symmetry axis through an angle ( $\phi$ ) of  $\pi$  radians (d) shows that the new equilibrium configuration could have been obtained from the original by inverting each nucleus in the centre of mass of the molecule

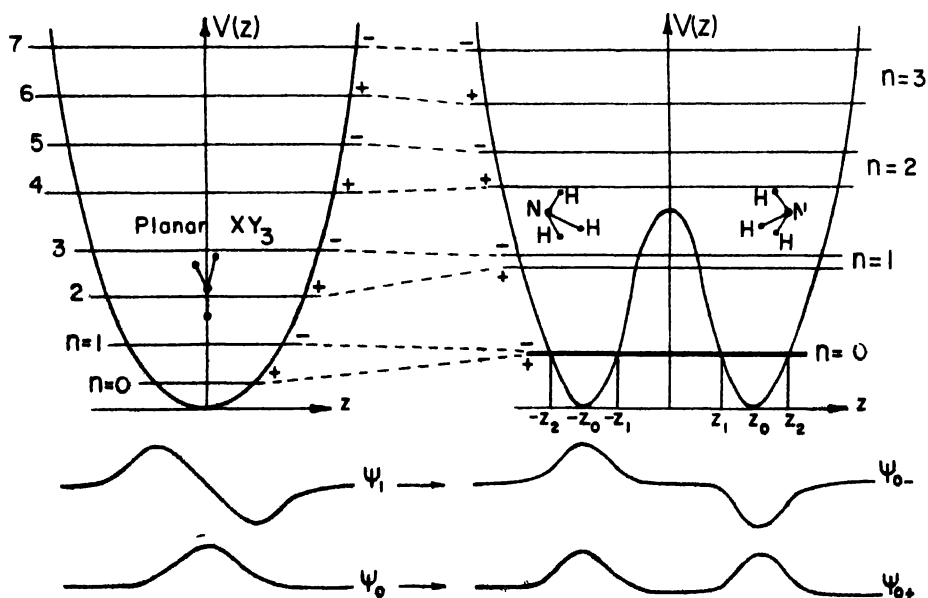


FIG. 7. Potential functions and energy levels for planar and pyramidal  $XY_3$  molecules. The wave functions for the two lowest states are shown below. The symmetry of the wave functions is not destroyed by the introduction of the potential hill.

either on one or the other side of the  $H_3$  plane, the  $NH_3$  potential function has the same symmetry as that of a planar  $XY_3$  molecule. If it is plotted as a function of  $z$ , the height of the central X nucleus above the  $Y_3$  plane, the potential of planar  $XY_3$  will have a minimum for  $z = 0$  (Fig. 7). The motion of the X particle in this parabolic potential corresponds to one of the normal modes of the  $XY_3$  molecule. The equally spaced energy levels are the vibrational energy levels for this mode, and because of the symmetry of the potential the wave functions are alternately even or odd functions of  $z$ . If this potential is slightly distorted by the addition of a very small hill in the centre, the energy levels are shifted by small amounts, the harmonic oscillator wave functions become slightly distorted; but in the ground state the central X nucleus still spends most of its time in or near the  $Y_3$  plane. As the height of the central hump is increased more and more the probability of finding the central nucleus in the plane  $z = 0$  becomes smaller and smaller. The maxima of the wave functions will occur near the two new minima of the potential which correspond to the two possible equilibrium configurations of a pyramidal  $XY_3$  molecule. Since the symmetry of the potential has not been destroyed, the wave functions still have the symmetry property (+) or (−) with respect to reflections in the plane  $z = 0$ . The energy levels approach each other in pairs, and as the barrier becomes large the wave functions for such a pair of levels become even or odd combinations respectively of harmonic oscillator functions for the vibrational motions in the two new potential wells (Fig. 7). The separation between such pairs of levels is governed by this vibrational frequency, the much smaller doublet splitting of each pair corresponds to the frequency with which the N atom tunnels through the potential barrier. For states very high above the potential hill the central hump again represents a small perturbation, and the energy levels approach the nearly equally spaced levels of a slightly hindered classical vibrational motion.

The AA approximation (Vol. I, Chapter 7) furnishes one of the simplest methods of estimating the doublet splitting of the lower energy states. The Schrödinger equation for the tunnelling motion can be written as

$$\frac{d^2\psi}{dz^2} + \frac{[P(z)]^2}{\hbar^2} \psi = 0 \quad (53)$$

where

$$[P(z)]^2 = 2\mu[E - V(z)]$$

$E$  is the total energy,  $\mu$  is the effective mass for the oscillation of the N atom against the  $H_3$  plane which has the value  $3mM/(3m + M)$  if the  $H_3$  triangle remains a rigid unit as the N passes through it,  $m$  is the mass of a hydrogen

atom and  $M$  is that of a nitrogen atom. In the classically forbidden region  $z > z_2$  (Fig. 7) the AA solution must have the form

$$\psi(z) = \frac{1}{(|P|)^{1/2}} \exp\left(-\frac{1}{\hbar} \int_{z_1}^z |P(\zeta)| d\zeta\right) \quad (z > z_2). \quad (54)$$

According to the connection formulas (Vol. I, Chapter 7, § 1.4) this exponentially decreasing solution approximates the same exact solution which in the oscillatory region,  $z_1 < z < z_2$ , has the approximate form

$$\psi(z) = \frac{2}{(P)^{1/2}} \cos\left(\frac{1}{\hbar} \int_{z_1}^z P(\zeta) d\zeta - \frac{J}{2\hbar} + \frac{\pi}{4}\right) \quad (55)$$

where

$$J = 2 \int_{z_1}^{z_2} [2\mu(E - V(z))]^{1/2} dz \cong J(E_0) + \left(\frac{\partial J}{\partial E}\right)_0 \delta E \quad (56)$$

and

$$E = E_0 + \delta E.$$

$E_0$  represents the average value of the energy of a pair of levels while  $\delta E$  gives the small shift of each level from  $E_0$  due to the tunnelling effect.  $J(E_0)$  is the action variable for an oscillator in a single well and must therefore have the value

$$J(E_0) = (n + \frac{1}{2})h, \quad (57)$$

while the derivative of the action with respect to the energy gives the period of this oscillator in its single well

$$\left(\frac{\partial J}{\partial E}\right)_0 = \frac{1}{\nu_0} \quad (58)$$

where  $\nu_0$  is the frequency of vibration in one of the potential minima. Making use of these relations and the connection formulas for the region of the classical turning point  $z_1$ , the above wave function can be matched to the appropriate AA solution in the region of the central hill

$$\psi(z) = \frac{(-1)^n}{(|P|)^{1/2}} \left\{ Q \cos\left(\frac{\pi \delta E}{h\nu_0}\right) \exp\left(+\frac{1}{\hbar} \int_0^z |P(\zeta)| d\zeta\right) - \right. \quad (59)$$

$$\left. \frac{2}{Q} \sin\left(\frac{\pi \delta E}{h\nu_0}\right) \exp\left(-\frac{1}{\hbar} \int_0^z |P(\zeta)| d\zeta\right) \right\} \quad (-z_1 < z < z_1)$$

where

$$Q = \exp \left( - \frac{1}{\hbar} \int_0^{z_1} [2\mu(V(z) - E)]^{1/2} dz \right). \quad (60)$$

This wave function must be an even or odd function of  $z$  for the (+) or (−) states respectively. From the behavior near  $z = 0$  we therefore get the result

$$\tan \left( \frac{\pi(\delta E)_{\mp}}{\hbar\nu_0} \right) = \pm \frac{Q^2}{2}. \quad (61)$$

Since the tunnelling shifts,  $\delta E$ , are small compared with the vibrational energy,  $\hbar\nu_0$ , the tunnel splitting of a pair of levels,  $\Delta$ , is given by

$$\Delta = (\delta E)_{-} - (\delta E)_{+} \cong (\hbar\nu_0/\pi)Q^2. \quad (62)$$

Since  $Q^2$  depends on the potential function  $V(z)$  only through the integral  $\int_0^{z_1} [2\mu(V - E)]^{1/2} dz$  the tunnel splitting is not a very sensitive function of the exact shape of the potential hill; but since  $Q^2$  is a small quantity which varies exponentially with the above integral, the splitting is a very sensitive function of the height of the barrier, the distance of the vibrational level below the top of the barrier, and the effective mass of the normal mode which corresponds to the tunnelling motion.

Although the height of the pyramid is changed somewhat in all of the normal modes of  $\text{NH}_3$  this change is extremely small in all of the modes except one. This is the mode in which the pyramid opens up like an umbrella and which can therefore be represented well by the one-dimensional motion of the N against the  $\text{H}_3$  plane. The drastic variations of the inversion splitting with  $(\mu)^{1/2}$  and  $(V - E)^{1/2}$  are illustrated by the observed splittings for this mode in  $\text{NH}_3$  and  $\text{ND}_3$  (Table IV).

TABLE IV  
OBSERVED INVERSION SPLITTINGS IN  $\text{NH}_3$  AND  $\text{ND}_3$ <sup>a</sup>

	$\text{NH}_3$	$\text{ND}_3$
Ground state	0.793 $\text{cm}^{-1}$	0.053 $\text{cm}^{-1}$
1st excited vibrational state	36.5 $\text{cm}^{-1}$	3.9 $\text{cm}^{-1}$
2nd excited vibrational state	312.5 $\text{cm}^{-1}$	70.0 $\text{cm}^{-1}$

<sup>a</sup> See Townes and Schawlow, "Microwave Spectroscopy," p. 306. McGraw-Hill, New York, 1955; and G. Herzberg, "Molecular Structure," Vol. II, p. 297. Van Nostrand, New York, 1945.

The potential function for the two isotopic species is the same, but the roughly twofold increase in the reduced mass of  $\text{ND}_3$  leads to approximately a tenfold decrease in the inversion splitting. The two levels for the second excited vibrational state of  $\text{NH}_3$  lie just above the top of the barrier. In this case the splitting approaches the separation between successive vibrational states. (The levels in Fig. 7 are drawn roughly to scale for  $\text{NH}_3$ . The separation of the lower levels corresponds to a vibrational frequency of  $950\text{ cm}^{-1}$ .)

The physical significance of the inversion splitting,  $\Delta$ , becomes apparent through a study of the time variations of the wave functions. For a vibrational state far below the top of the potential barrier the wave functions of the two inversion states can be written as the linear combinations

$$\begin{aligned}\psi_+ &= \frac{1}{\sqrt{2}}(\psi_L + \psi_R), \\ \psi_- &= \frac{1}{\sqrt{2}}(\psi_L - \psi_R)\end{aligned}\tag{63}$$

where  $\psi_L$  and  $\psi_R$  are vibrational wave functions for a single potential well corresponding to oscillations about the equilibrium configuration in which the N atom lies respectively to the left or to the right of the  $\text{H}_3$  plane (Fig. 7). If at time,  $t = 0$ , the N atom is found to the left of the  $\text{H}_3$  plane, the state of the system must be described by the wave function

$$\psi(z, t = 0) = \frac{1}{\sqrt{2}}(\psi_+(z) + \psi_-(z))\tag{64}$$

After a time  $t$  this wave function will have the form

$$\psi(z, t) = \frac{1}{\sqrt{2}}[\psi_+(z) + \psi_-(z) \exp\{-(2\pi i \Delta)t/h\}] \exp\{-(2\pi i E_+)t/h\}.\tag{65}$$

In particular, after a time  $t = h/2\Delta$  the wave function becomes

$$\psi\left(z, \frac{h}{2\Delta}\right) = \frac{1}{\sqrt{2}}[\psi_+(z) - \psi_-(z)] \exp\left[\frac{-(2\pi i E_+)t}{h}\right] = \psi_R \exp\left[\frac{-(2\pi i E_+)t}{h}\right]\tag{66}$$

i.e., the nitrogen atom is now found to the right of the  $\text{H}_3$  plane. The quantity  $\Delta/h$  therefore corresponds to the frequency with which the N tunnels back and forth through the  $\text{H}_3$  plane. In the ground state of  $\text{NH}_3$  the inversion of the molecule takes place with a frequency of  $23,786 \times 10^6$  times per second. In most other molecules the inversion frequency is too small to be observed. It has been estimated to have the value  $0.14 \times 10^6$  cps in the ground state of  $\text{PH}_3$  and  $\frac{1}{2}$  cycle per year in the ground state of  $\text{AsH}_3$ .<sup>13</sup>



It would therefore take two years for one complete tunnelling cycle of  $\text{AsH}_3$ , although the potential barrier of  $\text{AsH}_3$  has been estimated to be only 5.4 times that of  $\text{NH}_3$ .<sup>13</sup> These numbers illustrate the extreme sensitivity of the tunnelling frequency to the height of the potential barriers. In other non-planar molecules such as  $\text{CH}_3\text{Cl}$  the inversion may take billions of years, longer than the lifetime of the molecules in the universe.

The observed inversion splittings in the spectrum of  $\text{NH}_3$  are complicated by the rotational fine structure of the vibrational states. Each symmetric top rotational level is split into a (+) and a (−) level by the tunnelling phenomenon. The inversion of the nuclei *in the centre of mass* of the molecule is accomplished by a tunnelling of the N through the  $\text{H}_3$  plane followed by a rotation about the symmetry axis of the molecule through an angle of  $\pi$  radians [Fig. 6 (a)  $\rightarrow$  (b)  $\rightarrow$  (d)]; that is, by the transformation  $z = -z$ ,  $\phi \rightarrow \phi + \pi$ . It will be shown that the rotational wave function depends on the angle  $\phi$  only through the factor  $e^{\pm iK\phi}$  where the quantum number  $K$  is an integer so that the symmetry property of the states with respect to inversion in the centre of mass is given by the symmetry of the vibration-tunnel function multiplied by the factor  $(-1)^K$ . The (+) levels therefore form the lower levels of the inversion doublet for states with  $K$  even, while they form the upper levels for states with  $K$  odd. Since the electric dipole moment changes sign on inversion in the centre of mass the selection rule

$$+ \leftrightarrow -, \quad + \leftarrow | \rightarrow +, \quad - \leftarrow | \rightarrow -$$

must be added to the other symmetric top selection rules.

### 3.4 Rotational Hamiltonian

The rotational Hamiltonian of a polyatomic molecule which results from the approximate separation of rotation and vibration is one describing the free rotation of a rigid body, i.e., to this order of approximation the distances between the nuclei may be considered as fixed. It is expressed most simply in terms of the components of the total angular momentum  $\mathbf{P}$ , which in zeroth approximation is equal to the purely rotational angular momentum. Thus,

$$H = \frac{P_x^2}{2A} + \frac{P_y^2}{2B} + \frac{P_z^2}{2C} \quad (67)$$

where  $x, y, z$  are body-fixed axes along the three principal axes of inertia and  $A, B, C$  are the principal moments of inertia. In the quantum mechanical formulation the angular momentum components are replaced by operators which satisfy the commutation relations

$$P_\alpha P_\beta - P_\beta P_\alpha = -i\hbar P_\gamma \quad (68)$$

where  $\alpha, \beta, \gamma$  denote  $x, y, z$  cyclically. These differ from the usual angular momentum commutation relations only in the algebraic sign of the right-hand side. The commutation relations for the space-fixed components of the angular momentum have the usual form

$$P_a P_b - P_b P_a = +i\hbar P_c \quad (69)$$

where  $a, b, c$  denote cyclic permutations of  $X, Y, Z$  the axes of a right-handed space-fixed coordinate system.\* Matrix elements for such operators were described in Vol. I, Chapter 2, § 4 in a representation in which  $P^2$  and  $P_z$  are diagonal. The angular momentum eigenfunctions for the rigid top are simultaneous eigenfunctions of the commuting operators,  $P^2$ ,  $P_z$  and  $P_s$  and must be described in terms of three quantum numbers  $J$ ,  $M$ , and  $K$  where

$$P^2 \psi_{JKM} = \hbar^2 J(J+1) \psi_{JKM}; \quad P_s \psi_{JKM} = \hbar K \psi_{JKM}; \quad P_z \psi_{JKM} = \hbar M \psi_{JKM}. \quad (70a, b, c)$$

The matrix elements for the space-fixed components,  $P_a$ , which are diagonal in  $K$ , follow from the commutation relations (69) as previously. The matrix elements for the body-fixed components,  $P_\alpha$ , which are diagonal in  $M$ , have exactly the same form with the role of the quantum numbers  $M$  and  $K$  interchanged, except for a trivial change in phase arising from the minus sign in (68)

$$\begin{aligned} \langle JKM | P_s | J(K \pm 1)M \rangle &= (\hbar/2) [(J \mp K)(J \pm K + 1)]^{1/2}, \\ \langle JKM | P_y | J(K \pm 1)M \rangle &= \mp i(\hbar/2) [(J \mp K)(J \pm K + 1)]^{1/2}, \\ \langle JKM | P_x | JKM \rangle &= \hbar K. \end{aligned} \quad (71)$$

The angular momentum eigenfunctions can be expressed in terms of the three Euler angles describing the orientation of the molecule in space

$$\psi_{JKM} = \Theta_{JKM}(\theta) f_K(\phi) g_M(\psi) \quad (72)$$

where  $\phi$  is the angle of spin about the body-fixed  $z$ -axis,  $\psi$  is the azimuthal angle about the space-fixed  $Z$ -axis, and  $\theta$  is the tipping angle of the  $z$ -axis about the line of nodes. In terms of these coordinates, the eigenvalue equations (70b, c) become simply

$$\left(\frac{\hbar}{i}\right) \frac{\partial}{\partial \phi} f_K(\phi) = \hbar K f_K(\phi), \quad \left(\frac{\hbar}{i}\right) \frac{\partial}{\partial \psi} g_M(\psi) = \hbar M g_M(\psi). \quad (73)$$

Integration of these equations subject to the boundary condition that the

\* A derivation and discussion of the difference in algebraic sign of the commutation relations for the body- and space-fixed components has been given by Van Vleck.<sup>14</sup>

wave function be a single-valued function of the angles  $\phi$  and  $\psi$  gives the eigenfunctions

$$\psi_{JKM} = \left(\frac{N}{2\pi}\right) \Theta_{JKM}(\theta) e^{iK\phi} e^{iM\psi}, \quad (74)$$

with

$$K = 0, \pm 1, \pm 2, \dots, \pm J, \quad \text{and} \quad M = 0, \pm 1, \pm 2, \dots, \pm J.$$

### 3.5 Symmetric Top Molecules

If a molecule has an  $n$ -fold axis of symmetry, with  $n \geq 3$ , its inertial ellipsoid is a figure of revolution about the  $n$ -fold axis, ( $z$ ), so that the molecule has two equal principal moments of inertia,  $A = B$ . The rotational Hamiltonian of such a symmetric top can be written

$$H = \frac{(P^2 - P_z^2)}{2A} + \frac{P_z^2}{2C} \quad (75)$$

and  $H$  commutes with  $P^2$  and  $P_z$ . The angular momentum eigenfunctions, (72), are simultaneously the energy eigenfunctions, and the energy becomes

$$E_{JK} = \left(\frac{\hbar^2}{2A}\right) J(J+1) + \left(\frac{\hbar^2}{2}\right) \left(\frac{1}{C} - \frac{1}{A}\right) K^2. \quad (76)$$

Since the energy is independent of  $M$  and the sign of  $K$ , each level has a  $2(2J+1)$ -fold degeneracy, except for the states  $K=0$  which have only the  $(2J+1)$ -fold  $M$  degeneracy. If the symmetric top is of the prolate variety,  $A > C$ , as in a rod or cigar-shaped molecule, the  $J+1$  energy levels for a given value of  $J$  are increasing functions of  $K$ . If the symmetric top is oblate,  $A < C$ , as in a doughnut or disc shaped molecule, the energy levels for given  $J$  are decreasing functions of  $K$ .

The selection rules follow from the matrix elements of the space-fixed ( $X, Y, Z$ ) components of the electric dipole moment. Consider, for example,

$$\int \psi_A^* \mu_Z \psi_B d\tau = \int \psi_A^* [\mu_x \cos(x, Z) + \mu_y \cos(y, Z) + \mu_z \cos(z, Z)] \psi_B d\tau \quad (77)$$

in which  $\mu_x, \mu_y, \mu_z$ , the components of  $\mu$  along the body-fixed principal axes are given in terms of the permanent dipole moment and the normal coordinates by (33), and where the wave functions for the initial state  $A$  and final state  $B$  are products of zeroth order vibrational and rotational wave functions, e.g.,  $\psi_A = \psi_A^{\text{vib}} \psi_{J'K'M'}$ . In terms of the Euler angles the direction cosines are

$$\cos(x, Z) = \sin \theta \sin \phi, \quad \cos(y, Z) = \sin \theta \cos \phi, \quad \cos(z, Z) = \cos \theta \quad (78)$$

and the above matrix element can also be written as

$$\begin{aligned}
 & \int \psi_A^* \mu_z \psi_B d\tau \\
 &= \int \psi_A^{* \text{ vib}} \frac{1}{2} (\mu_x + i\mu_y) \psi_B^{\text{ vib}} d\tau_Q \int \psi_{J'K'M'}^* (-i \sin \theta e^{+\phi}) \psi_{J''K''M''} d\tau_{\theta\phi\psi} + \\
 & \int \psi_A^{* \text{ vib}} \frac{1}{2} (\mu_x - i\mu_y) \psi_B^{\text{ vib}} d\tau_Q \int \psi_{J'K'M'}^* (i \sin \theta e^{-\phi}) \psi_{J''K''M''} d\tau_{\theta\phi\psi} + \\
 & \int \psi_A^{* \text{ vib}} \mu_z \psi_B^{\text{ vib}} d\tau_Q \int \psi_{J'K'M'}^* \cos \theta \psi_{J''K''M''} d\tau_{\theta\phi\psi}.
 \end{aligned} \tag{79}$$

We must distinguish between two types of transitions. For a vibrational transition in which only the matrix element of  $\mu_z$  is different from zero, as in an  $A_1 \rightarrow A_1$  vibrational transition in  $\text{ClCH}_3$ , or in a pure rotational transition in which there is no change in the vibrational quantum number, the  $K$  selection rule becomes  $\Delta K = 0$  since the angular integral associated with  $\mu_z$  is independent of  $\phi$ . If the vibrational transition is such that one of the perpendicular components of  $\mu$ ,  $\mu_x$  or  $\mu_y$ , has a nonzero vibrational matrix element, as in an  $A_1 \rightarrow E$  transition in  $\text{ClCH}_3$ , then the  $K$  selection rule becomes  $\Delta K = \pm 1$ . It is important to note, however, that a transition  $\Delta K = -1$  ( $K'' = K' - 1$ ) is allowed only if

$$\int \psi_A^{* \text{ vib}} (\mu_x + i\mu_y) \psi_B^{\text{ vib}} d\tau_Q \neq 0$$

while a transition  $\Delta K = +1$  ( $K'' = K' + 1$ ) is allowed only if

$$\int \psi_A^{* \text{ vib}} (\mu_x - i\mu_y) \psi_B^{\text{ vib}} d\tau_Q \neq 0.$$

The space-fixed  $Z$  component of  $\mu$  also leads to the selection rule  $\Delta M = 0$ , (the rotational integrals are independent of the angle  $\psi$ ), while the  $X$  and  $Y$  components (not shown) lead to the selection rule  $\Delta M = \pm 1$  but make no changes in the  $K$  selection rules. The  $J$  selection rule,  $\Delta J = 0, \pm 1$ , follows from the general electric dipole selection rule for the total angular momentum.

There are thus two types of vibration-rotation bands in a symmetric top molecule, the parallel bands for which  $\Delta K = 0$  which are composed of simple  $P$ ,  $Q$ , and  $R$  branches corresponding to the selection rule  $\Delta J = -1, 0$ , and  $+1$  respectively, and the more complicated perpendicular bands for which  $K = \pm 1$ .

The frequencies for the parallel bands follow from (76)

$$\begin{aligned} P \text{ branch } \nu_{JK \rightarrow (J-1)K} &= \nu_{\text{vib}} - hJ/4\pi^2 A, \\ Q \text{ branch } \nu_{JK \rightarrow JK} &= \nu_{\text{vib}} \quad (J = 1, 2, \dots), \\ R \text{ branch } \nu_{(J-1)K \rightarrow JK} &= \nu_{\text{vib}} + hJ/4\pi^2 A. \end{aligned} \quad (80)$$

Such a band is illustrated by Fig. 4.

The perpendicular bands of a symmetric top arise from transitions to the doubly degenerate vibrational states belonging to the symmetry species  $E$ . These possess an internal angular momentum,  $p_z$ , directed along the symmetry axis of the molecule.\* Since the components of the total angular momentum along the principal axis are  $P_x$ ,  $P_y$  and  $P_z$ , the components of that part of the angular momentum due to the rotation of the molecule are  $P_x$ ,  $P_y$  and  $(P_z - p_z)$ . The rotational Hamiltonian is accordingly,

$$H = \frac{P_x^2 + P_y^2}{2A} + \frac{(P_z - p_z)^2}{2C} = \frac{P^2}{2A} + \frac{P_z^2}{2} \left( \frac{1}{C} - \frac{1}{A} \right) - \frac{P_z p_z}{C} + \frac{p_z^2}{2C}. \quad (81)$$

The internal angular momentum may be expressed in the usual manner in terms of the cartesian coordinates of the individual nuclei. These cartesian coordinates are fixed in the molecule and rotate with it. The operator

$$p_z = \left( \frac{\hbar}{i} \right) \sum_{k=1}^N \left( x_k \frac{\partial}{\partial y_k} - y_k \frac{\partial}{\partial x_k} \right) \quad (82)$$

must now be expressed in terms of the normal coordinates. For this purpose it is convenient to define mass-adjusted cartesian displacement coordinates

$$u_k = \sqrt{m_k} \Delta x_k, \quad v_k = \sqrt{m_k} \Delta y_k, \quad w_k = \sqrt{m_k} \Delta z_k \quad (83)$$

where  $m_k$  is the mass of the  $k$ th nucleus. The transformation from these coordinates to normal coordinates must be orthogonal since

$$T = \frac{1}{2} \sum_{k=1}^N (\dot{u}_k^2 + \dot{v}_k^2 + \dot{w}_k^2) = \frac{1}{2} \sum_{i=1}^{3N-6} \dot{Q}_i^2. \quad (84)$$

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\* It will be instructive for the student to consider the individual motions of the atoms of a molecule such as  $\text{CH}_3\text{Cl}$  for the doubly degenerate perpendicular vibrations. In such a vibration, the motions of the carbon and chlorine atoms, for example, lie in a plane perpendicular to the symmetry axis. By decomposing the motions into perpendicular harmonic oscillations differing in phase by  $90^\circ$  it is apparent that an internal angular momentum directed along the symmetry axis will result. See also ref. 1, Vol. II, p. 402.

As a result

$$\frac{\partial u_k}{\partial Q_i} = \frac{\partial Q_i}{\partial u_k}, \dots \quad (85a)$$

and

$$u_k = \sum_i \left( \frac{\partial u_k}{\partial Q_i} \right) Q_i = \sum_i \left( \frac{\partial Q_i}{\partial u_k} \right) Q_i \quad (85b)$$

so that the vibrational angular momentum operator becomes

$$p_z = \frac{\hbar}{i} \sum_{k=1}^N \left( u_k \frac{\partial}{\partial v_k} - v_k \frac{\partial}{\partial u_k} \right) \quad (86a)$$

$$= \frac{\hbar}{i} \sum_{i < j}^{3N-6} \left[ \sum_{k=1}^v \left( \frac{\partial Q_i}{\partial u_k} \frac{\partial Q_j}{\partial v_k} - \frac{\partial Q_i}{\partial v_k} \frac{\partial Q_j}{\partial u_k} \right) \right] \left( Q_i \frac{\partial}{\partial Q_j} - Q_j \frac{\partial}{\partial Q_i} \right)$$

$$p_z = \frac{\hbar}{i} \sum_{i < j}^{3N-6} \zeta_{ij}^{(z)} \left( Q_i \frac{\partial}{\partial Q_j} - Q_j \frac{\partial}{\partial Q_i} \right) \quad (86b)$$

where the "zetas" can be written in terms of a conventional abbreviation for the Jacobians

$$\zeta_{ij}^{(z)} = \sum_{k=1}^N \frac{\partial(Q_i, Q_j)}{\partial(u_k, v_k)}. \quad (86c)$$

The zetas are therefore constants which can be computed in terms of the force constants, the atomic masses, and the geometry of the molecule if the normal coordinate problem has been solved. If the normal coordinates  $Q_i$  and  $Q_j$  belong to different vibrational frequencies,  $\nu_i \neq \nu_j$ , the only nonzero matrix elements of the operator

$$\left( Q_i \frac{\partial}{\partial Q_j} - Q_j \frac{\partial}{\partial Q_i} \right)$$

are off-diagonal in the vibrational quantum numbers and can contribute to the energy only in higher order of approximation.\* If on the other hand  $(Q_{ia}, Q_{ib})$  belong to the same frequency  $\nu_i$ , in particular if the coordinates

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\* The matrix elements of  $p_z$  connecting vibrational states  $A$  and  $B$  can be different from zero only if the direct product based on  $\psi_A$  and  $\psi_B$  contains the irreducible representation of the  $z$  component of the pseudovector representation.

$(Q_{ix}, Q_{iy})$  are chosen to have the same transformation properties as the  $x$  and  $y$  components of a vector, the diagonal matrix elements of

$$\zeta_i \left( \frac{\hbar}{i} \right) \left( Q_{ix} \frac{\partial}{\partial Q_{iy}} - Q_{iy} \frac{\partial}{\partial Q_{ix}} \right)$$

will be different from zero and can contribute to the energy in first approximation.

It is convenient to transform the normal coordinates to two-dimensional polar coordinates

$$Q_{ix} = R_i \cos \chi_i, \quad Q_{iy} = R_i \sin \chi_i. \quad (87)$$

In terms of these the harmonic oscillator wave equation for a doubly degenerate normal coordinate becomes

$$-\frac{\hbar^2}{2} \left( \frac{\partial^2 \psi_i}{\partial R_i^2} + \frac{1}{R_i} \frac{\partial \psi_i}{\partial R_i} + \frac{1}{R_i^2} \frac{\partial^2 \psi_i}{\partial \chi_i^2} \right) + \frac{1}{2} \lambda_i R_i^2 \psi_i = E_i \psi_i \quad (88)$$

where the energy must have the value given previously

$$E_i = (n_i + 1) \hbar \nu_i. \quad (89)$$

Since  $\chi_i$  is an ignorable coordinate the wave function must have the form

$$\psi_{n_i, l_i}(R_i, \chi_i) = f_{n_i, l_i}(R_i) \exp(i l_i \chi_i) \quad (90)$$

where  $l_i$  must be a positive or negative integer. The substitution

$$f_{n_i, l_i} = \rho_i^{|l_i|} \exp(-\frac{1}{2} \rho_i^2) \sum_{k=0}^{\infty} a_k \rho_i^k \quad (91)$$

where  $\rho_i^2 = (\sqrt{\lambda_i}/\hbar) R_i^2$  leads to the recursion formula

$$a_{k+2} = \frac{2k + 2|l_i| - 2n_i}{(k+2)(k+2|l_i|+2)} a_k \quad (92)$$

and the requirement that the integers  $k$  be even. As a result the values of  $l_i$  are restricted to

$$\begin{array}{c} 0 \text{ for } n_i \text{ even} \\ \pm n_i, \pm (n_i - 2), \pm (n_i - 4), \dots, \pm 1 \text{ for } n_i \text{ odd.} \end{array}$$

The diagonal matrix elements of the vibrational angular momentum operator become simply

$$\iint \psi_{n_i, l_i}^* \hat{p}_\phi \psi_{n_i, l_i} R_i dR_i d\chi_i = \frac{\zeta_i}{2\pi} \int_{-\pi}^{\pi} \exp(-i l_i \chi_i) \frac{\hbar}{i} \frac{\partial}{\partial \chi_i} \exp(+i l_i \chi_i) d\chi_i = \hbar l_i \zeta_i. \quad (93)$$

For the fundamental vibrational state of a doubly degenerate frequency, the quantum numbers have the values,  $n_i = 1$ ,  $l_i = \pm 1$ , and the correction terms  $(-P_i p_i/C) + (p_i^2/2C)$  give the following correction to the rotational energy

$$E'_{1,\pm 1} = -\frac{\hbar^2 K(\pm 1)\zeta_i}{C} + \frac{\hbar^2 \zeta_i^2}{2C}. \quad (94)$$

Since the last term is independent of the rotational quantum numbers it is usually considered with the vibrational energy and omitted from the rotational energy, hence

$$E_{JKl_i = \pm 1} = \frac{\hbar^2}{2A} J(J+1) + \frac{\hbar^2}{2} \left( \frac{1}{C} - \frac{1}{A} \right) K^2 \mp \frac{\hbar^2}{C} K\zeta_i. \quad (95)$$

It has been shown that the transitions  $\Delta K = +1$  arise only from vibrational transitions for which the matrix element of  $(\mu_x - i\mu_y)$  is different from zero. In terms of the  $i$ th normal coordinate, this is,

$$(\mu_x - i\mu_y) = \left( \frac{\partial \mu_{\perp}}{\partial Q_i} \right)_0 (Q_{ix} - iQ_{iy}) = \left( \frac{\partial \mu_{\perp}}{\partial Q_i} \right)_0 R_i \exp(-i\chi_i). \quad (96)$$

It follows that the vibrational matrix element of  $(\mu_x - i\mu_y)$  connecting the ground state and the fundamental vibrational state  $n_i = 1$  is different from zero only if  $l_i = +1$ . Similarly, transitions  $\Delta K = -1$  which can arise only from the matrix element of  $(\mu_x + i\mu_y)$  are allowed only if  $l_i = -1$ . The selection rules for a perpendicular fundamental band of a symmetric top can therefore be summarized by

$$\Delta n_i = 1, \quad \Delta J = 0, \pm 1$$

either

$$\Delta K = +1, \quad \Delta l_i = +1 \text{ simultaneously}, \quad (97)$$

or

$$\Delta K = -1, \quad \Delta l_i = -1 \text{ simultaneously}.$$

The rotational structure of such a band is therefore complex and consists of 6 types of branches,  $P^R$ ,  $Q^R$ ,  $R^R$  for  $\Delta K = +1$  and  $P^P$ ,  $Q^P$ ,  $R^P$  for  $\Delta K = -1$ . The frequencies for the latter are:

$$\begin{aligned} P^P \text{ branch } \nu_{J,K \rightarrow J-1, K-1} = \nu_{\text{vib}} &- \frac{\hbar J}{4\pi^2 A} - \frac{\hbar}{4\pi^2} \left( \frac{1}{C} - \frac{1}{A} \right) (K - \tfrac{1}{2}) \\ &+ \frac{\hbar \zeta_i (K-1)}{4\pi C^2} \quad (J = K, K+1, \dots), \end{aligned}$$



$$Q^P \text{ branch } \nu_{J,K \rightarrow J,K-1} = \nu_{\text{vib}} - \left( \frac{h}{4\pi^2} \right) \left( \frac{1}{C} - \frac{1}{A} \right) (K - \tfrac{1}{2}) + \frac{h\zeta_s(K-1)}{4\pi^2 C}, \quad (98)$$

$$R^P \text{ branch } \nu_{J,K \rightarrow J+1,K-1} = \nu_{\text{vib}} + \frac{hJ}{4\pi^2 A} - \frac{h}{4\pi^2} \left( \frac{1}{C} - \frac{1}{A} \right) (K - \tfrac{1}{2}) \\ + \frac{h\zeta_s(K-1)}{4\pi^2 C} \quad (J = K + 1, K + 2, \dots).$$

Similar expressions give the branches arising from  $\Delta K = +1$ . Due to the superposition of the many  $J \rightarrow J$  transitions, the  $Q$  branches of the bands inherently give rise to the strongest lines and in general stand out above the background of the weaker individual  $P$  and  $R$  branch lines which may present a more or less irregular appearance due to the overlapping of the many  $P^P$ ,  $R^P$ ,  $P^R$ , and  $R^R$  branches. This situation obtains in the perpendicular bands of the methyl halides an example of which is shown in Fig. 5. The spacing between successive lines of the strong  $Q$  branches is equal to

$$\frac{h}{4\pi^2} \left( \frac{1 - \zeta_s}{C} - \frac{1}{A} \right) \quad (99)$$

Since the  $\zeta_s$  differ for the various normal vibrations, the spacings for the perpendicular fundamentals are in general not the same. The spacing of the  $Q$  branches in the overtone and combination bands of perpendicular type is discussed by Boyd and Longuet-Higgins.<sup>15</sup>

As mentioned previously the  $\zeta_s$  are functions of the force constants of the molecule. However, the sum of the zeta values for all the fundamentals in a particular irreducible representation is independent of the force field and is a function only of the geometrical configuration of the molecule. This sum rule will now be proved and the value of the zeta sum for molecules of the  $\text{ClCH}_3$  type will be derived.

The normal coordinates for a particular two-dimensional irreducible representation,  $\Gamma_i$ , can be built up from displacement coordinates,  $q_{ix}$ ,  $q_{iy}$ , which transform according to  $\Gamma_i$  in the same way as the normal coordinates  $Q_{ix}$ ,  $Q_{iy}$ . If the  $q_{ix}$ ,  $q_{iy}$  are chosen as orthonormal combinations of the  $3N$  mass-adjusted cartesian displacement coordinates,  $u_k$ ,  $v_k$ ,  $w_k$ , the representation  $\Gamma_i$  contributes a factor

$$\sum (\dot{q}_{ix}^2 + \dot{q}_{iy}^2) = \sum (\dot{Q}_{ix}^2 + \dot{Q}_{iy}^2)$$

to the kinetic energy. The potential energy will of course not be diagonal

in all the  $q_i$  though cross terms of the form  $q_{ix} q_{iy}$  will be missing. As a result the normal coordinates  $Q_{ix}, Q_{iy}$  are related to the  $q_{ix}, q_{iy}$  by

$$Q_{ix} = \sum_j \alpha_{ij} q_{jx}, \quad Q_{iy} = \sum_j \alpha_{ij} q_{jy} \quad (100)$$

where  $\alpha_{ij}$  is a real orthogonal matrix and where the number of possible values of  $i$  and the number of terms in the sums over  $j$  is equal to the number of vibrations, translations, and rotations in the irreducible representation,  $\Gamma_i$ . The zeta sum therefore has the value

$$\sum_i \zeta_i = \sum_i \sum_{k=1}^N \frac{\partial(Q_{ix}, Q_{iy})}{\partial(u_k, v_k)} = \sum_{ijl} \alpha_{ij} \alpha_{il} \sum_k \frac{\partial(q_{jx}, q_{ly})}{\partial(u_k, v_k)} \quad (101)$$

and making use of the orthogonality

$$\sum_i \zeta_i = \sum_i \sum_{k=1}^N \frac{\partial(q_{ix}, q_{iy})}{\partial(u_k, v_k)}. \quad (102)$$

The right-hand side of this expression must be independent of the force field since the symmetry coordinates  $q_{ix}, q_{iy}$  can be chosen in any arbitrary manner independent of the strengths of the molecular forces and consequently the sum rule is proved. However, in order to evaluate the sum of the  $\zeta_i$  for the *vibrations* in a particular irreducible representation we must subtract from the above sum the contributions of the translations and rotations that belong to that particular irreducible representation since the  $q_i$  are based on all  $3N$  degrees of freedom of the nuclei.

Figure 8 shows a set of orthonormal symmetry coordinates for an equilateral triangle made up of 3 identical atoms. The coordinates  $q_{1x}$ , and  $q_{2x}, q_{2y}$  would correspond to the actual normal vibrational coordinates of an  $X_3$  molecule, while the remaining symmetry coordinates would correspond to the translations and rotations of such a molecule. In a molecule of  $C_{3v}$  symmetry such as  $\text{ClCH}_3$  the normal coordinates would be linear combinations of the symmetry coordinates of Fig. 8 and the mass-adjusted cartesian displacement coordinates of the atoms situated on the figure axis of the molecule (e.g.,  $q_{4x} = u_4$ ,  $q_{4y} = v_4$  are of symmetry  $E$ ). The Jacobians for the irreducible representation,  $E$ , of the doubly degenerate modes may be evaluated from the expressions for  $q_{ix}, q_{iy}$  in Fig. 8. One obtains,

$$\sum_k \frac{\partial(q_{1x}, q_{1y})}{\partial(u_k, v_k)} = +1, \quad \sum_k \frac{\partial(q_{2x}, q_{2y})}{\partial(u_k, v_k)} = -1, \quad \sum_k \frac{\partial(q_{3x}, q_{3y})}{\partial(u_k, v_k)} = 0. \quad (103)$$

Also

$$\sum_k \frac{\partial(q_{4x}, q_{4y})}{\partial(u_k, v_k)} = \sum_k \frac{\partial(q_{5x}, q_{5y})}{\partial(u_k, v_k)} = +1.$$

The three equivalent off-axis atoms contribute zero to the zeta sum. This result holds for all sets of  $K$  equivalent atoms about a  $K$ -fold symmetry

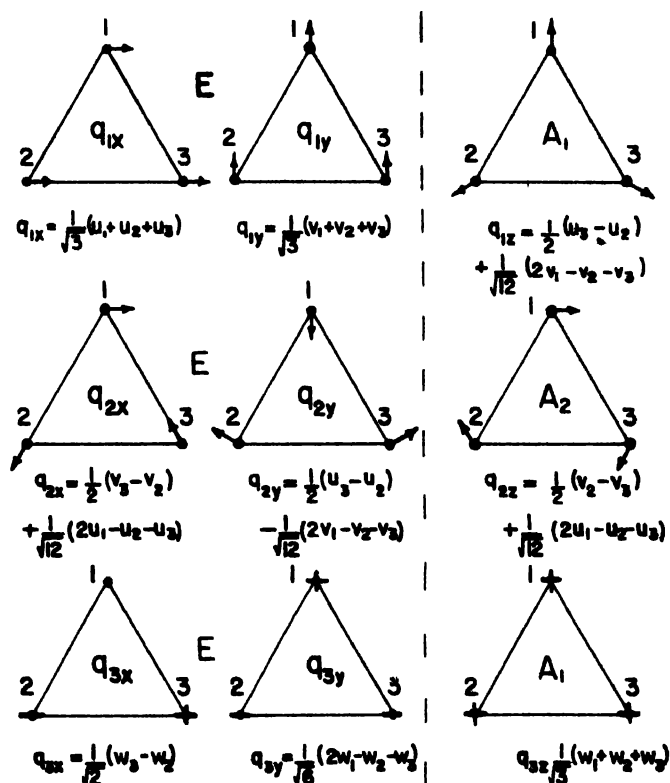


FIG. 8. Orthonormal symmetry coordinates for three equivalent atoms in a molecule of  $C_{3v}$  symmetry. The relative phases of the coordinates of symmetry  $E$  are chosen so that they all transform in the same way as the normal coordinates, e.g.

$$C_3 q_x = -\left(\frac{1}{2}\right)q_x + \left(\frac{\sqrt{3}}{2}\right)q_y; \quad C_3 q_y = -\left(\frac{\sqrt{3}}{2}\right)q_x - \left(\frac{1}{2}\right)q_y.$$

axis.<sup>15</sup> Each atom located on the 3-fold axis, however, contributes a factor  $+1$  so that  $\sum_i \zeta_i = n$  where  $n$  is the number of atoms situated on the 3-fold axis, but where the zeta sum still counts the effects of the translations and rotations. Since the translations  $t_x$ ,  $t_y$ , and the rotations  $r_x$ ,  $r_y$ , belong to the irreducible representation  $E$  in a  $C_{3v}$  molecule (Table II) their contribution

must still be subtracted from the sum. The translational and rotational symmetry coordinates  $t_x, t_y, r_x, r_y$  have the form

$$t_x = \sum_k (m_k/M)^{1/2} u_k, \quad t_y = \sum_k (m_k/M)^{1/2} v_k \quad (104a)$$

$$r_x = \sum_k (m_k/A)^{1/2} (y_k^{(0)} w_k - z_k^{(0)} v_k), \quad r_y = \sum_k (m_k/A)^{1/2} (z_k^{(0)} u_k - x_k^{(0)} w_k) \quad (104b)$$

where the coefficients have been chosen to normalize  $t_x, t_y, r_x, r_y$  in terms of the mass-adjusted cartesian displacement coordinates,  $u_k, v_k, w_k$ .  $M$  is the total mass of the molecule, and  $x_k^{(0)}, y_k^{(0)}, z_k^{(0)}$  define the equilibrium position of atom  $k$  relative to the centre of mass of the molecule. With these expressions we can compute

$$\sum_k \frac{\partial(t_x, t_y)}{\partial(u_k, v_k)} = \sum_k \begin{vmatrix} (m_k/M)^{1/2} & 0 \\ 0 & (m_k/M)^{1/2} \end{vmatrix} = +1, \quad (105a)$$

$$\sum_k \frac{\partial(r_x, r_y)}{\partial(u_k, v_k)} = \sum_k \begin{vmatrix} 0 & -(m_k/A)^{1/2} z_k^{(0)} \\ (m_k/A)^{1/2} z_k^{(0)} & 0 \end{vmatrix} = \sum_k \frac{m_k (z_k^{(0)})^2}{A} = 1 - C/2A. \quad (105b)$$

Subtracting these quantities from the sum  $\sum_i \zeta_i = n$  the zeta sum for the vibrational frequencies of symmetry  $E$  in a  $C_{3v}$  molecule is obtained

$$\sum_{i(\text{vib})} \zeta_i = n + \frac{C}{2A} - 2 \quad (106)$$

where  $n$  is the number of atoms on the 3-fold axis, for example  $n = 1$  for  $\text{NH}_3$ ,  $n = 2$  for  $\text{ClCH}_3$ , and  $n = 3$  for  $\text{NCCH}_3$ .

The zeta sum rule is of great practical value in determining the moments of inertia of a symmetric top molecule. The moment of inertia  $A = B$  may be readily found from the fine structure spacing of a parallel type band which as has been shown is equal to  $\hbar/4\pi^2 A$ . To the order of approximation in which vibration rotation interactions are neglected, all parallel type bands of a given molecule have the same spacing. The perpendicular type bands on the other hand will show different spacings of their  $Q$  branch lines since these depend upon the zetas which are in general not known. The sum of the spacings for the perpendicular fundamentals is, however, easy to interpret. Thus in  $\text{CH}_3\text{Cl}$  there are three perpendicular fundamentals,

$\nu_4$ ,  $\nu_5$ , and  $\nu_6$ . If the associated fine structure spacings  $\Delta\nu_4$ ,  $\Delta\nu_5$ , and  $\Delta\nu_6$ , (which are observed to be 8.28, 12.09 and  $6.95 \text{ cm}^{-1}$  <sup>16</sup>) are added one obtains,

$$\sum_{i=4}^6 \Delta\nu_i = \frac{h}{4\pi^2} \left[ \frac{(3 - \sum \zeta_i)}{C} - \frac{3}{A} \right] = \frac{h}{4\pi^2} \left[ \frac{3}{C} - \frac{7}{2A} \right] \quad (107)$$

by virtue of the zeta sum rule. Since the average fine structure spacing of the parallel bands of  $\text{CH}_3\text{Cl}$  has been observed to be  $0.876 \text{ cm}^{-1}$ , the inertial constants as well as the zetas may be calculated.  $A = B = 63.9 \times 10^{-40} \text{ gm cm}^2$ ,  $C = 5.53 \times 10^{-40} \text{ gm cm}^2$ ,  $\zeta_4 = 0.096$ ,  $\zeta_5 = -0.281$ ,  $\zeta_6 = 0.228$ .

Spherical top molecules such as methane where all three principal moments of inertia are equal,  $A = B = C$ , may be treated in a similar manner. It was shown (§ 3.2) that methane because of its high degree of symmetry possesses only four distinct vibrational frequencies. The non-degenerate fundamental,  $\nu_1$ , of species  $A_1$ , and the doubly degenerate fundamental,  $\nu_2$ , of species  $E$  are optically inactive. Only the two triply degenerate fundamentals,  $\nu_3$ ,  $\nu_4$ , of species  $F_2$  are infrared active. The classical motions of the active vibrational modes are therefore those of a three-dimensionally isotropic harmonic oscillator and must be expected to contribute a vibrational angular momentum along all three directions  $x$ ,  $y$ , and  $z$ . The zeroth-order rotational Hamiltonian must have the form

$$H = \frac{1}{2B} [(P_x - p_x)^2 + (P_y - p_y)^2 + (P_z - p_z)^2] = \frac{1}{2B} [\mathbf{P}^2 - 2\mathbf{P} \cdot \mathbf{p} + \mathbf{p}^2] \quad (108)$$

where the total angular momentum quantum vector  $\mathbf{P} = \hbar\mathbf{J}$  satisfies the basic angular momentum commutation relations with the minus sign (68), while the vibrational angular momentum vector,  $\mathbf{p}$ , in the  $i$ th vibrational state ( $i = 3$  or  $4$ ) has the value  $\zeta_i \hbar \mathbf{l}$  where the quantum vector  $\hbar \mathbf{l}$  commutes with  $\mathbf{P}$  and satisfies the basic angular momentum commutation relations with a plus sign (69). It follows that the resultant of the quantum vector  $\mathbf{P}$  and the quantum vector  $(-\hbar \mathbf{l})$  satisfies the commutation relations (68) so that this resultant quantum vector,  $\hbar \mathbf{J}_i$ , which gives the angular momentum of the rotating molecular framework, is such that

$$\mathbf{J}_i^2 = J_i(J_i + 1) \quad \text{with} \quad J_i = (J + l), \dots, |J - l|,$$

while its projection on the molecular symmetry axis is specified by the quantum number  $K_i$ , ( $K_i = +J_i, \dots, -J_i$ ). The rotational energy in the  $i$ th fundamental vibrational state has the value

$$E = \frac{\hbar^2}{2B} J(J + 1) - \frac{\hbar^2}{B} \zeta_i (\mathbf{J} \cdot \mathbf{l}) + \frac{\hbar^2}{2B} \zeta_i^2 l(l + 1) \quad (109)$$

where

$$(\mathbf{J} \cdot \mathbf{l}) = \frac{1}{2}[J(J+1) + l(l+1) - J_l(J_l+1)]. \quad (110)$$

In the vibrational ground state,  $l = 0$ , and the rotational energy becomes simply

$$E = \frac{\hbar^2}{2B} J(J+1) \quad (111)$$

where the state  $J$  has a degeneracy  $g_J = (2J+1)^2$ , one factor  $(2J+1)$  coming from the possible orientations of  $\mathbf{J}$  in space,  $(M)$ , the other from the  $(2J+1)$  possible orientations in the molecule,  $(K)$

In a triply degenerate vibrational fundamental state  $l = 1$ , (with a corresponding projection quantum number  $m_l = +1, 0, -1$ ), and  $J_l$  can have the values  $(J+1)$ ,  $J$ , or  $(J-1)$ . A state of total angular momentum  $J$  thus splits into three components. The rotational energies  $E(J, l=1, J_l)$  have the three possible values:

$$\begin{aligned} E(J, 1, J+1) &= (\hbar^2/2B) J(J+1) + \hbar^2 \zeta_l J/B + \hbar^2 \zeta_l^2/B, \\ E(J, 1, J) &= (\hbar^2/2B) J(J+1) - \hbar^2 \zeta_l B + \hbar^2 \zeta_l^2/B, \\ E(J, 1, J-1) &= (\hbar^2/2B) J(J+1) - \hbar^2 \zeta_l (J+1)/B + \hbar^2 \zeta_l^2/B \end{aligned} \quad (112)$$

The correct zeroth order wave functions for the state  $(J, l=1, J_l)$  are given through the angular momentum addition or Clebsch-Gordan coefficients (Chapter 1, § 7.3, in this volume) by

$$\psi_{K_l}(J, 1, J_l) = \sum_{\substack{m \\ (K = K_l - m)}} \langle JK1m | J1J_l K_l \rangle \psi_{JK} \psi_{1m} \quad (113)$$

where the  $\psi_{JK}$  are the eigenfunctions of  $\mathbf{P}$ , namely the symmetric top wave functions of (72) (the quantum number  $M$  has been suppressed to avoid confusion), while the  $\psi_{1m}$  are the eigenfunctions of  $l=1$  which are linear combinations of three-dimensionally isotropic harmonic oscillator wave functions.

It can be shown<sup>16</sup> that the selection rule  $\Delta J = +1$  must be accompanied by the selection rule  $\Delta J_l = -1$ ,  $\Delta J = 0$  by  $\Delta J_l = 0$ , and  $\Delta J = -1$  by  $\Delta J_l = +1$ . As a result the rotational lines of the single  $P$  and  $R$  branches ( $\Delta J = -1$  and  $+1$  respectively) of the active fundamentals  $\nu_3$  and  $\nu_4$  show the constant spacing  $\Delta\nu_i = (\hbar/4\pi^2 B)(1 - \zeta_i)$ ,  $i = 3$  or  $4$ . There exists a sum rule which may be shown to be  $\zeta_3 + \zeta_4 = \frac{1}{2}$ . Thus from the observed spacings in methane  $\Delta\nu_3 = 9.93 \text{ cm}^{-1}$ , and  $\Delta\nu_4 = 5.74 \text{ cm}^{-1}$ , one calculates from  $\Delta\nu_3 + \Delta\nu_4 = (\frac{1}{2})\hbar/4\pi^2 B$  that  $B = 5.23 \times 10^{-40} \text{ gm cm}^2$  and  $\zeta_3 = 0.05$ ,  $\zeta_4 = 0.45$ .

## 3.6 Asymmetric Top Molecules

If a molecule has no 3-fold or higher-fold axis of symmetry the three principal moments of inertia  $A, B, C$  are in general all different. The water molecule ( $\text{H}_2\text{O}$ ) is an example of such an asymmetric top. The rotational Hamiltonian (67) can be rearranged and written in the form

$$H = \frac{1}{4A} + \frac{1}{4B} (P_x^2 + P_y^2) + \frac{P_z^2}{2C} + \left( \frac{1}{4A} - \frac{1}{4B} \right) (P_x^2 - P_y^2) \quad (114)$$

where the first terms have the form of the symmetric top Hamiltonian and the last term gives the effect of the asymmetry. In the limiting case of the symmetric top,  $B = A$ , the Hamiltonian commutes with the operators  $P^2$  and  $P_z$ , (as well as with  $P_z$  the space-fixed  $Z$  component of the angular momentum), and the angular momentum eigenfunctions  $\psi_{JKM}$  of (74) are simultaneously the energy eigenfunctions of the symmetric top. In the asymmetric case, however, the Hamiltonian  $H$  no longer commutes with  $P_z$ , although it does commute with  $P^2$ , (and with  $P_z$ ). As a result the energy eigenfunctions are linear combinations of the  $2J + 1$  wave functions  $\psi_{JKM}$  with different values of  $K$ , but with the same values of  $J$  and  $M$ . In a representation based on the symmetric top wave functions  $\psi_{JKM}$  the Hamiltonian has matrix elements off-diagonal in  $K$  and must therefore be transformed to a new representation in which it will be diagonal. The energy levels may be found in the usual manner by setting the so-called secular determinant equal to zero  $|H_{ij} - E\delta_{ij}| = 0$  where  $i, j$  denote the quantum numbers  $JKM$  of the symmetric top representation. The matrix elements of  $P_x^2$  and  $P_y^2$  can be found from the matrix elements (71) for  $P_x$  and  $P_y$ , by matrix multiplication, and lead to the following as the only nonvanishing matrix elements for the Hamiltonian

$$\begin{aligned} \langle JKM | H | JKM \rangle &= \hbar^2 \left( \frac{1}{4A} + \frac{1}{4B} \right) J(J+1) + \hbar^2 K^2 \left( \frac{1}{2C} - \frac{1}{4A} - \frac{1}{4B} \right), \\ \langle JKM | H | J(K \pm 2)M \rangle &= \left( \frac{\hbar^2}{8} \right) \left( \frac{1}{A} - \frac{1}{B} \right) [(J \mp K)(J \mp K - 1)(J \pm K + 1)(J \pm K + 2)]^{1/2}. \end{aligned} \quad (115)$$

Since the matrix elements are diagonal in  $J$  the secular determinant factors into a series of subdeterminants, one for each value of  $J$ , of order  $2J + 1$ , corresponding to the  $2J + 1$  values of  $K$ , and the energy levels for a particular value of  $J$  are given by the  $2J + 1$  roots of the determinantal equation. These will in general be distinct except in the limiting cases where  $A = B$ , or  $B = C$ . (Since the matrix elements are independent of  $M$  the  $2J + 1$   $M$ -degeneracy is not removed.)

There is no convenient quantum number having simple physical significance by which the  $(2J + 1)$  distinct energy levels for a particular value of  $J$  can be designated, and the levels are designated simply by  $J_\tau$ , where the index  $\tau$  is an integer ranging from  $-J$  to  $+J$  which indicates the ordering of the levels for a given  $J$ . Thus  $J_J$  represents the highest,  $J_{J-1}$  the next highest, and  $J_{-J}$  the lowest energy level with total angular momentum quantum number  $J$ . The levels may also be specified by the quantum numbers  $K$  of the two limiting symmetric top energy levels,  $A = B$  and  $B = C$ . Let the moments of inertia be ordered in the following way,  $C \geq B \geq A$ , and imagine that the intermediate moment of inertia,  $B$ , ranges from the values  $B = A$  to  $B = C$ . In the limit  $B = A$  the molecule is an oblate symmetric top, the Hamiltonian matrix (115) is diagonal, and the symmetric top quantum number  $K$  is a "good quantum number." (It is commonly designated  $K_1$ .) If  $B$  is slightly different from  $A$ , the small asymmetry splits the levels  $\pm K_1$  which are degenerate in the oblate symmetric top limit. The energy levels for  $J = 3$  are plotted as a function of  $B$  in Fig. 9. As the value of  $B$  increases the asymmetry splitting increases. In the other extreme, as  $B$  approaches  $C$ , the energy levels go over to the levels of a prolate symmetric top. In the limit  $B = C$  the Hamiltonian matrix is again diagonal but in a representation in which the matrix elements of  $P_x$  are diagonal. These have the values  $\hbar K_{-1}$ , where the prolate symmetric top quantum number  $K_{-1}$  again has integral values from  $-J$  to  $+J$ . Since each oblate symmetric top level goes over continuously to one of the prolate symmetric top levels as  $B$  ranges from  $A$  to  $C$ , the asymmetric top levels with total angular momentum  $J$  can also be specified by giving the values  $K_{-1}$  and  $K_1$  of the two limiting symmetric top levels, and the states are often designated by  $J_{K_{-1}K_1}$ . (The ordering index  $\tau$  is equal to  $K_{-1} - K_1$ ).

The actual mechanics of diagonalizing the Hamiltonian for a given value of  $J$  can be simplified by making use of the symmetry of the problem. The off-diagonal matrix elements of the Hamiltonian (115) in the oblate symmetric top representation connect only states for which  $K$  (i.e., the oblate symmetric top quantum number  $K_1$ ) differ by 2 units. As a result there can be no connection between states of even and odd  $K$ , and the  $2J + 1$  by  $2J + 1$  secular determinant splits further into 2 subdeterminants, while the energy eigenfunctions are expandable in series of symmetric top wave functions using *either* even values of  $K$  only *or* odd values only.

$$\psi_{J\tau M}(E) = \sum_K' S_{K\tau}(J) \psi_{JKM} \quad (116)$$

where the prime indicates that the sum is *either* over all possible even *or*



over all possible odd values of  $K$ . Since the symmetric top wave functions (74) depend on the quantum number  $K$  only through the factor  $e^{iK\phi}$ , they undergo the transformation  $\psi_{JKM} \rightarrow (-1)^K \psi_{JKM}$  under rotation through

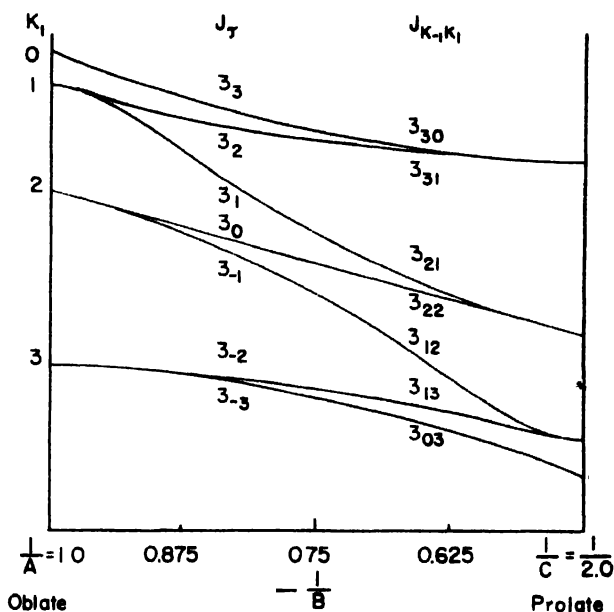


FIG. 9. Energies of the asymmetric top levels with total angular momentum,  $J = 3$ . The principal moments of inertia  $C$  and  $A$  are assumed to have the values  $A = 1$ ,  $C = 2$ , in arbitrary units. The plots show the positions of the seven energy levels as  $B$  ranges from  $B = A$ , the oblate symmetric top limit at the left, to  $B = C$ , the prolate symmetric top limit at the right. (Note that the asymmetry splitting of a nearly symmetric top is very small when  $K \simeq J$ . The lower energy levels occur in closely spaced pairs for the nearly oblate symmetric top, while the upper energy levels occur in closely spaced pairs for the nearly prolate symmetric top. For the fully developed asymmetric top ( $1/B = 0.75$ ), both the high and the low energy states occur in symmetrical pairs about the more widely spaced central levels. Note also the symmetry of the whole level scheme about the midpoint of the  $\tau = 0$  level.)

$180^\circ$  about the  $z$ -axis, the axis of the greatest moment of inertia,  $C$ , and it follows that the energy eigenfunctions  $\psi_{J\tau M}(E)$  for states involving even  $K$  (i.e., even  $K_1$ ) are symmetric (+) while the states involving odd  $K$  only are antisymmetric (−) with respect to such a rotation, ( $C_{2C}$ ). From Fig. 9 it can be seen that the highest state  $\tau = J$  for any given value of  $J$  is symmetric (+) with respect to such rotations about the  $C$ -axis since it must go over to the state  $K_1 = 0$  in the oblate symmetric top limit, and since the symmetry of the wave function must be independent of the actual value of the moments of inertia. (A small change in the moments of inertia corresponds to a perturbation which cannot change the symmetry of the wave

function.) The two next highest levels  $\tau = J - 1$  and  $J - 2$  associated with the limiting quantum number  $K_1 = 1$  are antisymmetric ( $-$ ), the next two ( $+$ ), etc. Similar consideration of the energy eigenfunctions in terms of the limiting prolate symmetric top wave functions shows that the wave function for a state for which  $K_{-1}$  is even is symmetric ( $+$ ) with respect to rotations through  $180^\circ$  about the  $x$ -axis, the axis of the least moment of inertia,  $A$ , while states with  $K_{-1}$  odd are antisymmetric ( $-$ ) with respect to such rotations, ( $C_{2A}$ ). As a result the lowest state  $\tau = -J$  for any value of  $J$  is always ( $+$ ) with respect to  $C_{2A}$ , the next two,  $\tau = -J + 1$  and  $-J + 2$ , are ( $-$ ), the next two ( $+$ ), etc.

The symmetries of the wave functions are indicated in Fig. 10 for states with  $J = 3$  and  $J = 2$ . The symmetry properties of the wave functions reflect the symmetry of the rotational Hamiltonian which is unchanged by a rotation through  $180^\circ$  about any principal axis of inertia even though the molecular configuration itself may not be invariant to such a rotation. Under rotation about the  $z$ -axis,  $C_{2C}$ , for example,  $P_z \rightarrow +P_z$ ,  $P_x \rightarrow -P_x$ ,  $P_y \rightarrow -P_y$ , leaving the Hamiltonian (114) unchanged. The asymmetric top rotational wave functions must thus transform according to the irreducible representations of the four-group ( $D_2$ ), the group of symmetry operations including besides the identity operation the rotations about three mutually orthogonal twofold axes,  $C_{2C}$ ,  $C_{2B}$ ,  $C_{2A}$ . Since a rotation through  $180^\circ$  about the  $y$ -axis, the axis of the intermediate moment of inertia,  $C_{2B}$ , is equivalent to successive rotations about the  $z$ - and  $x$ -axes,  $C_{2C}$  and  $C_{2A}$ , the symmetry of the wave function under  $C_{2B}$  is given by the products of the symmetries under  $C_{2C}$  and  $C_{2A}$ . The four-group has only 4 irreducible representations. They are denoted by  $(++)$ ,  $(+-)$   $(-+)$ , and  $(--)$  where the symbols indicate the symmetry properties under the operations  $C_{2C}$  and  $C_{2A}$  in that order.

Since the energy eigenfunctions must transform according to one of the four irreducible representations of the four-group, and since the matrix elements of the Hamiltonian can be different from zero only if they connect states of the same symmetry, the secular determinant for any value of  $J$  will break into four independent determinants if the matrix elements of the Hamiltonian are evaluated in a representation based on a set of  $2J + 1$  wave functions of appropriate symmetry. The transformation coefficients  $S_{K\tau}(J)$  of (116), which depend on  $J$  and in general are functions of the moments of inertia, are the elements of the unitary matrix  $S$  which diagonalizes the Hamiltonian,  $(S^{-1}HS)_{\tau\tau'} = E_\tau \delta_{\tau\tau'}$ . The unitary matrix  $S$  can be factored into two parts  $S = S_1 S_2$ , where  $S_1$  transforms from the oblate symmetric top representation to a representation based on wave

functions of appropriate symmetry, so that the diagonalization of the transformed Hamiltonian ( $S_1^{-1}HS_1$ ) by means of  $S_2$  will involve the diagonalization of four separate matrices, one for each irreducible representation of the four-group, where only the four factors of  $S_2$  will be functions of  $A$ ,  $B$ , and  $C$ .

It can be seen that the following linear combinations of the oblate symmetric top wave functions

$$\psi_{JKM}^{\pm} = \frac{1}{\sqrt{2}} (\psi_{JKM} \pm \psi_{J-KM}) \quad (117)$$

transform according to one of the irreducible representations of the fourgroup.

Under the transformation  $C_{2C}$ , or  $\phi \rightarrow \phi + \pi$ , the symmetric top wave functions undergo the transformation

$$C_{2C} \psi_{JKM} = (-1)^K \psi_{JKM} \quad (118)$$

A rotation,  $C_{2A}$ , about the  $A$ -axis, is equivalent to a reversal of the  $C$ -axis,  $\theta \rightarrow \pi - \theta$ ,  $\psi \rightarrow \psi + \pi$  followed by a rotation about the  $C$ -axis  $\phi \rightarrow \pi - \phi$  (if  $\phi$  is measured from the  $A$ -axis). From a detailed knowledge of the angular dependence of the rotational wave functions  $\psi_{JKM}$  it can be shown that this rotation transforms the wave functions according to

$$C_{2A} \psi_{JKM} = (-1)^J \psi_{J-KM} \quad (119)$$

The linear combinations (117) therefore have the transformation properties

$$C_{2C} \psi_{JKM}^{\pm} = (-1)^K \psi_{JKM}^{\pm} \quad \text{and} \quad C_{2A} \psi_{JKM}^{\pm} = \pm (-1)^J \psi_{J-KM}^{\pm} \quad (120)$$

so that  $\psi_{JKM}^{-}$  with  $J$  and  $K$  both odd, for example, transforms according to the irreducible representation  $(-+)$ . The symmetric top wave function  $\psi_{J0M}$  transforms according to  $(++)$  for  $J$  even and  $(+-)$  for  $J$  odd. If the symmetric top wave functions are expressed in terms of a row matrix with  $K = -J, -J+1, \dots$  in that order, the  $(2J+1) \times (2J+1)$  matrix

$$S_1 = \left\| \begin{array}{cccccc} -\frac{1}{\sqrt{2}} & 0 & \cdot & 0 & 0 & \frac{1}{\sqrt{2}} \\ 0 & -\frac{1}{\sqrt{2}} & \cdot & 0 & \cdot & \frac{1}{\sqrt{2}} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \cdot & 1 & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & \frac{1}{\sqrt{2}} & \cdot & 0 & \cdot & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & 0 & \cdot & 0 & 0 & \frac{1}{\sqrt{2}} \end{array} \right\| \quad (121)$$

transforms the matrix elements of the Hamiltonian to a representation based on the wave functions (117) of appropriate symmetry. The matrix elements of  $S_1^{-1}HS_1$  for  $J = 2$  are shown in Table V.

TABLE V

$JKM^\pm$	$22M^-$	$21M^-$	$20M$	$21M^+$	$22M^+$
$22M^-$	$a + b + 4c$	0	0	0	0
$21M^-$	0	$a + 4b + c$	0	0	0
$20M$	0	0	$3a + 3b$	0	$\sqrt{3}(a - b)$
$21M^+$	0	0	0	$4a + b + c$	0
$22M^+$	0	0	$\sqrt{3}(a - b)$	0	$a + b + 4c$

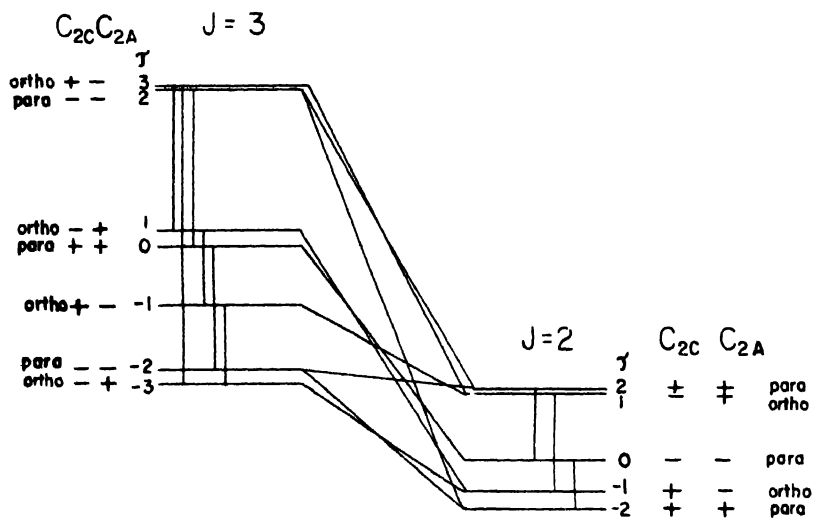


FIG 10. The states  $J = 2$  and  $J = 3$  for the  $H_2O$  molecule ( $A = 1.01$ ,  $B = 1.93$ ,  $C = 3.01 \times 10^{-40}$  gm cm<sup>2</sup>), showing the symmetries of the states and the pure rotational transitions. The permanent electric dipole moment lies along the  $B$ -axis. The transitions indicated are also the allowed transitions for the vibration-rotation bands for the fundamentals  $\nu_1$  and  $\nu_2$  for which the change of electric dipole moment lies along the  $B$ -axis, provided one of the states involved in a transition is the vibrational ground state while the other is one of the states  $\nu_1$  or  $\nu_2$ . (The symmetries under  $C_{2C}$  are always given by  $+ - - + + - - \dots$  starting with the highest level  $\tau = J$ , while the symmetries under  $C_{2A}$  are  $+ - - + + - - \dots$  starting with the lowest level  $\tau = -J$ . In  $H_2O$  the population of the ortho-states is greater than that of the para-states by a factor of 3 (§ 3.7).

These have been computed through (115) and (121) where the abbreviations  $a = \hbar^2/2A$ ,  $b = \hbar^2/2B$ ,  $c = \hbar^2/2C$  have been used. Note also that  $S_1^{-1} = S_1$ . The matrix breaks up into four submatrices, three  $1 \times 1$  matrices corresponding to the levels of symmetry  $(+ -)$ ,  $(- -)$ , and  $(- +)$  in that order, and a single  $2 \times 2$  matrix for the two  $(+ +)$  states (cf. Fig. 10). Further diagonalization of the  $2 \times 2$  matrix gives the following energy values for the five  $J = 2$  states

$$\begin{aligned} E_{++} &= 2(a + b + c) \pm 2[(a - c)(a - b) + (b - c)^2]^{1/2}, \\ E_{+-} &= a + b + 4c, \\ E_{--} &= a + 4b + c, \\ E_{-+} &= 4a + b + c. \end{aligned} \quad (122)$$

From Fig. 10 it can also be seen that the Hamiltonian matrix for  $J = 3$  factors into a single  $1 \times 1$  matrix, for the  $(+ +)$  state, and three independent  $(2 \times 2)$  matrices for the  $(+ -)$ ,  $(- -)$ , and  $(- +)$  states. For higher values of  $J$  the dimensions of certain of the submatrices will be  $\geq 3$  and the corresponding energy values are roots of cubic and higher degree equations and are best evaluated numerically.<sup>17</sup>

The selection rules follow from the form of the wave functions and their symmetry. Since the energy eigenfunctions are linear combinations of symmetric top wave functions involving the same  $J$  and  $M$ , the selection rules  $\Delta J = 0, \pm 1$ ,  $\Delta M = 0, \pm 1$  are carried over from the symmetric top wave functions. In general, if the equilibrium configuration of the molecule has some symmetry (as in  $H_2O$ , for example) the electric dipole moment, or its change during one of the normal vibrations, must lie along one of the principal axes of inertia of the molecule leading to additional symmetry selection rules. In water vapor ( $H_2O$ ), for example, the permanent electric dipole moment must lie along the molecular symmetry axis which is the axis of the intermediate moment of inertia  $B$ , (the molecule has the structure of an obtuse isosceles triangle, H-O-H angle =  $104.5^\circ$ ). The dipole moment will therefore reverse direction under the transformations  $C_{2C}$  and  $C_{2A}$  while it remains unchanged under  $C_{2B}$ . The transition probabilities are given by the matrix elements of the space-fixed components of the electric dipole moment

$$\mu_G = \int \psi_{J'\tau'M'}^* \mu_B \cos(B, G) \psi_{J\tau M} d\Omega \quad (123)$$

where  $\cos(B, G)$  is the direction cosine between the molecule-fixed  $B$ -axis and any space-fixed  $G$ -axis. Since  $\mu_B \cos(B, G)$  changes sign under the transformations  $C_{2C}$  and  $C_{2A}$ , the integral is different from zero only if the product  $\psi_{J'\tau'M'}^* \psi_{J\tau M}$  also changes sign under both operations  $C_{2C}$  and  $C_{2A}$ .

that is, if the final state wave function transforms according to the opposite sign from the initial state wave function for both symmetry operations. We must thus add the selection rule:

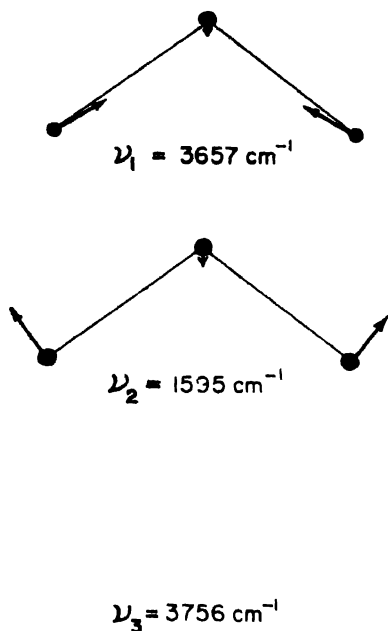


FIG. 11. The normal vibrations and observed fundamental frequencies of water vapor,  $\text{H}_2\text{O}$

(1) If the dipole moment (or its change) lies along the axis of the intermediate moment of inertia,  $B$ , only the transitions

$$++ \leftrightarrow --$$

and  $+- \leftrightarrow -+$  are allowed.

By similar arguments one obtains also the selection rules:

(2) If the dipole moment (or its change) lies along the axis of the smallest moment of inertia,  $A$ , only the transitions

$$++ \leftrightarrow -+$$

and  $+- \leftrightarrow --$  are allowed,

(3) If the dipole moment (or its change) lies along the axis of the greatest moment of inertia,  $C$ , only the transitions

$$++ \leftrightarrow ++$$

and  $-+ \leftrightarrow -+$  are allowed

The allowed transitions of the pure rotational spectrum of water vapor involving states  $J = 2$  and  $J = 3$  are illustrated in Fig. 10.

The water molecule possesses three fundamental bands whose frequencies and normal modes of vibration are shown in Fig. 11. Clearly the change of electric moment lies along the intermediate or  $B$ -axis for  $\nu_1$  and  $\nu_2$  and therefore these bands will have similar fine structures (see Fig. 10). In  $\nu_3$  however the change of electric moment lies along the least or  $A$ -axis and the fine structure is predicted and observed to differ from that of the other two fundamentals. All fine structures including that of the pure rotation spectrum are exceedingly complex and irregular. In spite of this complexity it has been possible to identify each individual line and consequently to determine the rotation and the rotation-vibration levels of the molecule. The actual unravelling of the spectrum has been made especially difficult since the rotation-vibration interactions are relatively large and must be considered in predicting the positions of the lines.

### 3.7 Symmetry Properties and the Exclusion Principle: Nuclear Spin

The symmetry properties of a polyatomic molecule, in general, arise from the fact that the molecule possesses two or more identical nuclei which are situated in equivalent positions. The existence of identical particles in a system leads to the exclusion of many states otherwise possible for nonidentical particles. Thus if the particles possess integral spin (including zero) only those states will occur whose wave functions are unchanged for an interchange of any pair of identical particles (Bose-Einstein statistics). On the other hand if the particles have half odd integer spin, the only states to occur are those whose wave functions change sign only for an interchange of identical particles (Fermi-Dirac statistics).

The total wave function must have the properties just listed but the individual wave functions (electronic, vibration, rotation and nuclear spin) may have any properties subject only to the limitation on their product:\*

$$\psi_{\text{total}} = \psi_{\text{el}} \psi_{\text{vib}} \psi_{\text{rot}} \psi_{\text{spin}}$$

Since the ground state electronic wave functions of almost all polyatomic molecules are totally symmetrical they have the properties of an identity operator, and consequently may be omitted from the further discussion.

Consider first the molecule  $\text{H}_2\text{O}$  as an example of a system containing two identical nuclei. The normal modes of vibration are shown in Fig. 11. If the normal coordinates are designated  $q_1$ ,  $q_2$ , and  $q_3$  respectively, a rotation of the molecule about the twofold symmetry axis which interchanges the hydrogen nuclei will transform  $q_1 \rightarrow q_1$ ,  $q_2 \rightarrow q_2$ , but  $q_3 \rightarrow -q_3$ . The vibrational wave functions  $\psi_{n_1}(q_1)$  and  $\psi_{n_2}(q_2)$  thus belong to the symmetric irreducible representation,  $A$ , for all values of  $n_1$  and  $n_2$ .  $\psi_{n_3}(q_3)$  is an even function of  $q_3$  for  $n_3$  even, and odd for  $n_3$  odd. This follows rigorously since the vibrational Hamiltonian is necessarily invariant if  $q_3 \rightarrow -q_3$ . Collecting these results, it is clear that  $\psi_{\text{vib}}$  is symmetric (species  $A$ ) for  $n_3$  even and antisymmetric (species  $B$ ) for  $n_3$  odd.<sup>†</sup>

\* Strictly speaking the system does not completely separate and consequently writing  $\psi$  as a product is only an approximation although generally a very good one. However the symmetry does not depend upon the magnitude of interaction terms and hence the results to be obtained are rigorous.

<sup>†</sup> The Hamiltonian is invariant under the symmetry operations of the point group  $C_{2v}$ . However, only the rotational subgroup  $C_2$  need be considered since the 2-fold rotation about the symmetry axis is the only symmetry operation which interchanges the two identical nuclei. The two irreducible representations (or species) of the group  $C_2$  are commonly designated  $A$  and  $B$ .

The symmetry properties of the rotational part of the wave function will depend on the coordinate transformation which interchanges the identical nuclei. In water vapor the H-O-H apex angle is relatively obtuse,  $104.5^\circ$ , and consequently the hydrogen nuclei lie along a line parallel to the least principal axis of inertia. A symmetry operation which interchanges the identical nuclei is a rotation of  $180^\circ$  about the intermediate axis of inertia. This is equivalent to the products of  $C_{2A}$  and  $C_{2C}$  and therefore the states with symbols  $(++)$  and  $(--)$  belong to species  $A$ , while  $(+-)$  and  $(-+)$  are  $B$ , or antisymmetric states. A study of the distribution of the species shows that in water vapor the rotational states of species  $A$  and  $B$  have respectively even and odd values of the quantum number  $\tau$ .\*

The symmetry properties of the nuclear spin part of the wave function for two identical nuclei have already been treated in the discussion of the homonuclear diatomic molecule. If the spin has a magnitude  $I$  there exist  $(2I + 1)^2$  states. Of these  $(2I + 1)(I + 1)$  are of species  $A$  and  $(2I + 1)I$  of species  $B$ .

These results may be combined readily and will be illustrated by considering the ground electronic and vibrational states of  $H_2O$  and  $D_2O$ . The symmetry species of the total wave function  $\psi = \psi_{el} \psi_{vib} \psi_{rot} \psi_{spin}$  is given by the direct product of the symmetry species of the individual wave functions. Clearly  $A \times A = B \times B = A$  while  $A \times B = B$ . In the case of  $H_2O$ ,  $I = \frac{1}{2}$  and the total wave function must be of species  $B$ . The ground electronic and vibrational wave functions are both  $A$ . Multiplying the rotational and spin wave functions it is evident that the rotational states  $(++)$  and  $(--)$  are multiple with weight  $(2J + 1)(2I + 1)^2 = 4(2J + 1)$ . Of these three  $(2J + 1)$  are  $A$  states and  $(2J + 1)$  are  $B$ . In the same way the levels  $(+-)$  and  $(-+)$  are divided into  $(2J + 1)$   $A$  states and three  $(2J + 1)$   $B$  states. Since only the  $B$  states occur in nature, the populations of the  $(+-)$  and  $(-+)$  states will be greater than the  $(++)$  and  $(--)$  states by a factor of three. These populations comprise the ortho- and para-states of  $H_2O$ . Transitions between them will be extremely feeble and can be brought about only by interactions with the nuclear spins.

It will be remembered that the pure rotational transitions for  $H_2O$  connect states  $(++) \leftrightarrow (--)$  and  $(+-) \leftrightarrow (-+)$ . The latter will

\* It should be remarked that if the apex angle had been smaller (in fact, less than  $86.6^\circ$  in the case of  $H_2O$ ) the identical nuclei would have lain along the middle axis of inertia, and the relevant operations would have been the product of  $C_{2B}$  and  $C_{2C}$  which is equal to  $C_{2A}$ . Thus  $(++)$  and  $(-+)$  would belong to species  $A$  and  $(+-)$  and  $(--)$  to  $B$ .



accordingly be enhanced relative to the former by a factor of three. This enhancement is observed. The reader can complete the discussion by considering the fine structure of the vibration bands and should note the difference between the fundamental  $\nu_3$  and the fundamentals  $\nu_1$  or  $\nu_2$ .

The situation for  $D_2O$  is altered only in that here  $I = 1$  and the total wave function must be of species  $A$ . An analysis shows that the states  $(++)$  and  $(--)$  are more heavily populated than  $(+-)$  and  $(-+)$  by a factor of two.

A discussion of molecules having a threefold axis of symmetry such as  $NH_3$  or  $CH_3Cl$  may be made in a similar manner. It will again be assumed (as is in fact the case for these molecules) that the ground electronic wave function belongs to  $A_1$ , the totally symmetric irreducible representation, of the point group  $C_{3v}$ .

It is convenient to divide the vibrational part of the wave function into two factors, an inversion function and a normal vibration function. The effect of the possibility of inversion has been shown to split each level into two levels of which one belongs to species  $A_1$  and the other to  $A_2$ . In the case of  $CH_3Cl$ , in contrast to that of  $NH_3$ , the tunnelling process is so slow — it may require many years — that the separation between members of a pair is entirely unobservable. The inversion levels may then be considered as forming a virtually coincident pair of species  $A_1, A_2$ .

The normal vibration portion of the wave function has symmetry properties which have been discussed earlier. The ground state as well as the excited states of the parallel vibrations all belong to species  $A_1$ . The first excited states of the perpendicular vibrations on the other hand are doubly degenerate and of species  $E$ . The higher excited states of the perpendicular modes have symmetry properties which may be obtained by a simple extension of the discussion already given. The results may be stated rather simply. A perpendicular vibration with principal quantum number  $n$  has been shown to have an azimuthal number  $l$  where  $|l| = n, n - 2, n - 4$ , etc. The symmetry depends solely upon  $l$ . For  $l = 0$  the species is  $A_1$ , for  $l \neq 0$  but not a multiple of 3, the species is  $E$ , while for  $l \neq 0$  and a multiple of 3 there are two levels,  $A_1$  and  $A_2$ , which in principle might be slightly separated by an anharmonic perturbation.

The symmetry properties of the rotational wave functions are independent of the spatial quantum number  $M$  so that only a pair of symmetric top wave functions  $\psi_{JKM}, \psi_{J-KM}$  need be considered for a particular state  $J, K (K \neq 0)$ . Since the symmetric top wave functions depend on  $\phi$ , the azimuth angle about the symmetry axis, only through the factor  $e^{iK\phi}$ , a rotation through

$2\pi/3$  about the figure axis transforms the rotational wave functions according to

$$\begin{pmatrix} C_3 \psi_{JKM} \\ C_3 \psi_{J-KM} \end{pmatrix} = \begin{pmatrix} e^{2\pi i K/3} & 0 \\ 0 & e^{-2\pi i K/3} \end{pmatrix} \begin{pmatrix} \psi_{JKM} \\ \psi_{J-KM} \end{pmatrix} \quad (124)$$

Under the symmetry operation  $C_3$  the character of the representation based on the rotational eigenfunctions for state  $J, K$  thus have the value  $-1$ , provided  $K$  is not a multiple of 3. If  $K$  is a multiple of 3, however, it has the value  $+1$ . A reflection in one of the symmetry planes which interchanges

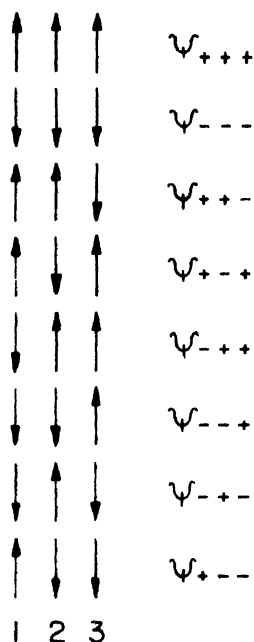


FIG. 12. Possible spin orientations and spin wave functions of three identical nuclei with spin  $I = \frac{1}{2}$ .

one pair of identical particles in  $\text{NH}_3$  and  $\text{CH}_3\text{Cl}$  is equivalent to a tunnelling through a plane normal to the 3-fold axis followed by a rotation through  $180^\circ$  about an axis normal to the 3-fold axis. (See Fig. 6a  $\rightarrow$  b  $\rightarrow$  c.) The symmetry property of the wave function due to the first part of this process has already been accounted for by the inversion function. The symmetry property of the rotational wave function under a rotation about an axis normal to the figure axis has been discussed in § 3.6. It is  $\psi_{JKM} \rightarrow (-1)^J \psi_{J-KM}$ . The character of the representation based on  $(\psi_{JKM}, \psi_{J-KM})$  is thus equal to zero for this transformation for all values of  $K$ , ( $K \neq 0$ ). From the values of the characters it can be seen from Table II of § 3.2 that the rotational wave functions belong to species  $E$  if  $K$  is not a multiple of 3 and  $K \neq 0$ ; while, if  $K$  is a multiple of 3, and  $K \neq 0$ , there are two levels (to a high approximation coincident) of species  $A_1$  and  $A_2$ . If  $K=0$  the rotational wave function has symmetry  $A_1$  for  $J$  even,  $A_2$  for  $J$  odd. Since the inversion

levels form a virtually coincident pair of species  $A_1$  and  $A_2$  in almost all molecules ( $\text{NH}_3$  and  $\text{ND}_3$  are of course exceptions) the distinction between  $A_1$  and  $A_2$  rotational states is of no importance in general, and the symmetry properties of the rotational wave functions differ essentially only in their dependence upon  $K$ .

The nuclear spin wave function may also be decomposed into the various species  $A_1$ ,  $A_2$ , and  $E$ . If each of the three equivalent nuclei has a spin  $I$ , each spin may be oriented in  $(2I + 1)$  ways in an external magnetic field

and consequently there will exist  $(2I + 1)^3$  individual wave functions. The manner in which these combine in symmetry species will be illustrated for the case of  $I = \frac{1}{2}$ . The resulting eight orientations and wave functions are shown in Fig. 12. From the character of the representation,  $\Gamma_I$ , based on these 8 nuclear spin functions we can obtain in the usual way the number of functions which transform according to each irreducible representation. Under one of the rotations about the 3-fold axis, e.g., under the permutation (123), only the two functions  $\psi_{+++}$ ,  $\psi_{---}$  remain unchanged and contribute the factor +1 to the diagonal of the transformation matrix. All other functions transform into one another and contribute only off-diagonal matrix elements (e.g.  $\psi_{-++} \rightarrow \psi_{+-+}$ ), so that the character  $\chi_I$  for the symmetry operation  $C_3$  has the value  $\chi_I(C_3) = 2$ . Under reflection in one of the symmetry planes, for example the one containing atom 1, that is under the permutation (1) (23),\* the four functions  $\psi_{+++}$ ,  $\psi_{+--}$ ,  $\psi_{--+}$ ,  $\psi_{-++}$  remain invariant, so that  $\chi_I(\sigma) = 4$ . Finally  $\chi_I(E) = 8$ , the dimension of the representation (The characters of the representation  $\Gamma_I$  are shown in Table II). A reduction of  $\Gamma_I$  into its irreducible components by the usual methods gives

$$\Gamma_I = 4A_1 + 2E$$

It can also be seen by direct inspection that the wave functions

$$\begin{aligned} \psi_I(A_1) &= \psi_{+++} & \psi_{III}(A_1) &= \frac{1}{\sqrt{3}} (\psi_{+--} + \psi_{-+-} + \psi_{--+}) \\ \psi_{II}(A_1) &= \psi_{---} & \psi_{IV}(A_1) &= \frac{1}{\sqrt{3}} (\psi_{-++} + \psi_{+-+} + \psi_{++-}) \\ \left. \begin{aligned} \psi_{Vx}(E) \\ \psi_{Vy}(E) \end{aligned} \right\} &= \begin{aligned} &\frac{1}{\sqrt{2}} (\psi_{+-+} - \psi_{+--}) \\ &\frac{1}{\sqrt{6}} (2\psi_{-++} - \psi_{+-+} - \psi_{++-}) \end{aligned} \\ \left. \begin{aligned} \psi_{VIx}(E) \\ \psi_{VIy}(E) \end{aligned} \right\} &= \begin{aligned} &\frac{1}{\sqrt{2}} (\psi_{-+-} - \psi_{--+}) \\ &\frac{1}{\sqrt{6}} (2\psi_{+--} - \psi_{-+-} - \psi_{--+}) \end{aligned} \end{aligned} \quad (125)$$

have the symmetry indicated

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\* The permutation (1) (23) is said to consist of two cycles, while (123) consists of a single cycle, and the identity operation (1) (2) (3) is a three-cycle operation.

The characters for the representation  $\Gamma_I$  in the general case where the nuclear spin is  $I$  are also shown in Table II. In general, the character  $\chi_I(R)$  for the symmetry operation  $R$  is equal to  $(2I + 1)^k$  where  $k$  is equal to the number of cycles in the permutation corresponding to  $R$ . It follows from the reduction that

$$\Gamma_I = \frac{1}{3}(2I + 1)(2I^2 + 5I + 3)A_1 + \frac{1}{3}(2I + 1)(2I^2 - I)A_2 + \frac{2}{3}(2I + 1)(I^2 + I)E$$

As a self-consistency check it will be noted that the sum of the number  $A_1$ ,  $A_2$  and twice the  $E$  species is equal to  $(2I + 1)^3$ , as it must. (Twice the number of  $E$  species must be taken since the  $E$  species are doubly degenerate.)

To find the symmetry species of the total wave function it is only necessary to employ the direct products

$$A_1 \times A_1 = A_2 \times A_2 = A_1, \quad A_1 \times A_2 = A_2, \quad A_1 \times E = A_2 \times E = E,$$

and  $E \times E = A_1 + A_2 + E$ . Consider as an example a vibrational state of  $\text{CH}_3\text{Cl}$  belonging to the species  $A_1$ . These include any excited state made up from the parallel vibrations alone ( $\nu_1$ ,  $\nu_2$  or  $\nu_3$ ) as well as the ground vibration state itself. Multiplying the normal vibration and the inversion wave functions one obtains the two levels  $A_1$  and  $A_2$ . Since the nuclear spin of the proton  $I = \frac{1}{2}$ , the spin wave function consists of  $4A_1 + 2E$ . Thus the product of all the wave functions excluding only the rotation is  $4A_1 + 4A_2 + 4E$ . Multiplying now by the rotational wave function one finds,

$$\begin{array}{lll} K = 0 & \text{states} = 4A_1 + 4A_2 + 4E & \text{weight} = 4(2J + 1), \\ |K| = 3n \pm 1 & \text{states} = 4A_1 + 4A_2 + 12E & \text{weight} = 4(2J + 1), \\ |K| = 3n & \text{states} = 8A_1 + 8A_2 + 8E & \text{weight} = 8(2J + 1) \end{array}$$

The protons with their half integer spin must obey Fermi-Dirac statistics, that is, only  $A_2$  states will occur. (Since a rotation about the 3-fold axis is equivalent to *two* successive interchanges of pairs of protons the total wave function must remain unchanged under this symmetry operation, that is, it must be of  $A$  type. Further, only wave functions of  $A_2$  symmetry change sign under interchange of only a single pair of identical nuclei.) The weight of a state is therefore equal to the number of  $A_2$  levels multiplied by the usual rotational weight factor  $2J + 1$ .\*

It is evident that for the vibrational levels of  $\text{CH}_3\text{Cl}$  under discussion the statistics imposes the condition that those rotational states where  $K$

\* When  $K \neq 0$  the rotational weight is usually given as  $2(2J + 1)$ , the factor 2 corresponding to the two possibilities  $+K$  and  $-K$ . In the present discussion this double possibility has already been accounted for in enumerating the species.

is a multiple of three will be enhanced by a factor of 2. Transitions between these vibrational levels result in the parallel type bands where  $K \rightarrow K$ ,  $J \rightarrow J$  or  $J \pm 1$ . Each fine structure line is therefore a superposition of lines for which  $K = 0, 1 \dots J - 1$ . The superposition largely averages out the enhancement factor on the individual  $K$  levels (except perhaps for low values of  $J$ ) and consequently the fine structure lines show no marked alternations.

In the case of a perpendicular fundamental the observed fine structure consists of the  $Q$  branches for which  $K \rightarrow K \pm 1$  and  $J \rightarrow J$ . Here it is expected that every third line will be enhanced by a factor 2. This enhancement is evident in Fig. 5 although the method of observation does not yield a quantitative measure of its amount.

The appearance of a perpendicular band with every third  $Q$  branch line enhanced may be inferred, as has been done, by considering only the weights of the ground vibration state levels. To be complete however one should also examine the weights of the excited levels and show that they are consistent with the considerations already given.

In a fundamental vibrational state of one of the doubly degenerate modes of symmetry  $E$  the interaction between the vibrational and rotational angular momentum, as has been shown earlier, splits each state  $J$ ,  $|K|$  into a lower level of 2-fold degeneracy ( $+|K|$ ,  $l = +1$ ), ( $-|K|$ ,  $l = -1$ ), and an upper level ( $+|K|$ ,  $l = -1$ ), ( $-|K|$ ,  $l = +1$ ) of similar 2-fold degeneracy. ( $\zeta_i$  is assumed to be positive for the specific band under discussion.) The vibrational wave function  $\psi_{(n_i=1), (l_i=\pm 1)}$  has the same transformation properties as  $(\dot{q}_{4x} + iq_{4y})$  for  $l_i = +1$ , and as  $(q_{4x} - iq_{4y})$  for  $l_i = -1$ , where  $q_{4x}$  and  $q_{4y}$  are the cartesian displacement vectors of an atom located on the 3-fold axis (such as atom 4 of  $\text{ClCH}_3$ ). From Fig. 3 it can be seen that

$$C_3(q_{4x} + iq_{4y}) = e^{-2\pi i/3} (q_{4x} + iq_{4y}),$$

$$C_3(q_{4x} - iq_{4y}) = e^{+2\pi i/3} (q_{4x} - iq_{4y})$$

while the rotational wave function transforms according to

$$C_3 e^{i|K|\phi} = e^{2\pi i|K|/3} e^{i|K|\phi}.$$

Combining these transformation properties we see that the lower states have symmetry  $E$  for  $|K| = 2, 3, 5, 6, 8, 9, \dots$  while they may be further split into  $A_1$  and  $A_2$  levels for  $|K| = 1, 4, 7, \dots$ . The upper states on the other hand have symmetry  $E$  for  $|K| = 1, 3, 4, 6, 7, 9, 10, \dots$  while they in turn may be further split into  $A_1$  and  $A_2$  components for  $|K| = 2, 5, 8, \dots$ . The single  $K = 0$  levels are of symmetry  $E$ .

Combining the vibration, inversion, rotation, and nuclear spin wave functions, and remembering that for  $\text{CH}_3\text{Cl}$  the final species must be  $A_1$ , one readily arrives at the following result. For the lower levels resulting from the vibration rotation interaction the states  $|K| = 2, 3, 5, 6, 8, 9, \dots$  have the weight  $4(2J + 1)$ , while the states  $|K| = 1, 4, 7, \dots$  have weight  $8(2J + 1)$ . For the upper levels, the states  $|K| = 1, 3, 4, 6, 7, \dots$  have weight  $4(2J + 1)$ , and  $|K| = 2, 5, 8, \dots$  have weight  $8(2J + 1)$ . The single level  $K = 0$  has weight  $4(2J + 1)$ . Since the selection rules are  $\Delta l = +1$ ,  $\Delta|K| = +1$ , and  $\Delta l = -1$ ,  $\Delta|K| = -1$ , inspection shows that the radiative transitions connect states having the same statistical weight formulas. The above discussion which has been somewhat specialized for  $\text{CH}_3\text{Cl}$  may be readily generalized for any symmetrical top molecule having three identical nuclei. It may also be applied to the interesting case of  $\text{NH}_3$  where the inversion levels are so widely separated that the lines resulting from transitions to each level may be individually observed.

# 5. Elements of Quantum Statistics

D. ter Haar

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## 1. Introduction

Although in many fields of physics quantum mechanics has introduced essentially new features, statistical mechanics was by its very nature suited to incorporate the transition from classical to quantum mechanics without changing its formalism. Under statistical mechanics, or thermostatics to use a term coined by Kramers,<sup>1</sup> we understand that branch of physics which attempts to derive the properties of matter in bulk from the properties of the constituent particles. The transition to quantum mechanics is taken care of by the change in the atomic properties, that is, by such aspects as symmetry requirements of the wave function of the system, a Schrödinger equation to describe the internal motion of a diatomic molecule instead of canonical equations of motion, discrete energy levels instead of an energy continuum, and so on. The derivation of macroscopic properties is then obtained by statistical methods which are the same for the classical as for the quantum case. The commonly used term "quantum statistics" is thus,

to a large extent, a misnomer as the statistics are not affected by quantum rules — they are only applied to particles which are described quantum mechanically rather than classically.

In the present chapter we shall be concerned only with quantum systems, but from what was stated above it follows that we must first study the methods of statistical mechanics in general before specializing our interest. This will be done in § 1; we shall, however, consider the special form of the statistical formalism applicable to quantum systems. In § 1.3, § 2, and § 3 we shall apply these methods to relatively simple quantum systems. It is clear that in the limited space of one chapter we can touch only very briefly upon the topics discussed, while many topics are completely left out. For a more detailed discussion of statistical mechanics we must refer to the literature<sup>2-5</sup>; for obvious reasons we shall often refer to “Elements of Statistical Mechanics”<sup>5</sup> for more details, and we shall quote it as ESM in the following.

### 1.1 The Elementary Method of Statistical Mechanics

Although in all physical systems the constituent particles will be interacting, there are many cases where, to a fair approximation, we can treat the system under consideration as a collection of noninteracting particles. (We have elsewhere<sup>6,7</sup> discussed the fact that the noninteracting particles are not necessarily the constituent particles, but often have the character of “quasi particles.”) For our present discussion it is sufficient that such physical systems as the conduction electrons in a metal, the lattice vibrations of a crystal, or ferromagnetic excitations (the so-called spin-waves) can be described by using the formulas for a collection of independent particles, at least to a first approximation. We shall therefore discuss in the present subsection a method — called in ESM the elementary method of statistics — which can be used for such systems. In § 1.2 we shall discuss the more general case of interacting particles; moreover, for the present we shall consider systems with only one kind of particle, a restriction to be lifted also in § 1.2.

We consider a system of  $N$  independent, identical particles. In that case the Hamiltonian  $H$  of the system will be the sum of the Hamiltonians  $h$ , of the individual particles,

$$H = \sum h, (p_k^{(i)}, q_k^{(i)}). \quad (1)$$

In Eq. (1) the summation is over all particles in the system,  $p_k^{(i)}$  and  $q_k^{(i)}$  stand for the  $s$  ( $k = 1, \dots, s$ ) generalized momenta and coordinates, where  $s$  is the number of degrees of freedom per particle, and all  $h$ , are identical



functions of their arguments. If  $E$  and  $\psi$  are respectively the total energy of the system and its wave function, the time-independent Schrödinger equation for the system will be

$$\mathbf{H}\psi = E\psi. \quad (2)$$

Because of the form (1) of the Hamiltonian we can use the method of separation of variables and find eigenfunctions of  $\mathbf{H}$  of the form

$$\psi = \prod \psi(i) \quad (3)$$

corresponding to an energy eigenvalue

$$E = \sum \varepsilon(i), \quad (4)$$

where  $\psi(i)$  and  $\varepsilon(i)$  are the eigenfunctions and energy eigenvalues of the single particle Schrödinger equation,

$$\mathbf{h}_i \psi_m(i) = \varepsilon_m \psi_m(i). \quad (5)$$

In Eq. (5)  $\psi_m(i)$  is the eigenfunction belonging to the  $m$ th eigenstate of the  $i$ th particle with energy  $\varepsilon_m$ . We have written here  $\psi_m(i)$  for  $\psi_m(q_k^{(i)})$  and  $\varepsilon_m$  for  $\varepsilon_m(i)$ .

A stationary state of the system can be characterized by giving the number of particles occupying the different single-particle eigenstates. If there are  $n_m$  particles in the  $m$ th stationary state, the wave function of the system will be of the following form

$$\psi = \psi_1(1)\psi_1(2)\dots\psi_1(n_1)\psi_2(n_1+1)\psi_2(n_1+2)\dots\psi_2(n_1+n_2)\psi_3(n_1+n_2+1)\dots, \quad (6)$$

where we have numbered the particles starting from those occupying the first stationary state.

The state of the system corresponding to the wavefunction (6) looks highly degenerate — even if we assume that there are no accidental degeneracies due to linear relations with integer coefficients between the  $\varepsilon_m$  — since apart from the  $\psi$  given by Eq. (6) all  $P\psi$  given by the equation

$$P\psi = \psi_1(k_1)\psi_1(k_2)\dots\psi_1(k_{n_1})\psi_2(k_{n_1+1})\dots\psi_2(k_{n_1+n_2})\psi_3(\dots)\dots \quad (7)$$

will also be eigenfunctions of the system belonging to the same energy eigenvalue. In (7) the numbers  $k_1, k_2, \dots, k_{n_1}, \dots, k_{n_1+n_2}$  are a permutation  $P$  of the numbers  $1, 2, \dots, i, \dots, N$ .

There are situations where this degeneracy is real, namely, those where we have means to distinguish between the  $N$  different particles, for instance, when we are dealing with a crystalline system where although the particles

are indistinguishable, the lattice points are not, and we can distinguish the particles by the lattice site they occupy. In such a case the degree of degeneracy, or weight,  $W(n_m)$  of a distribution of the particles over the various particle eigenstates characterized by the  $n_m$  will be proportional to the number of ways in which  $N$  particles can be distributed in such a way that there are  $n_1$  particles in the first eigenstate,  $n_2$  in the second, . . . . One finds [ESM § 4.2]

$$W_{\text{Bo}}(n_m) = \prod [n_m!]^{-1}. \quad (8)$$

The reason for the index "Bo" will be discussed presently.

The majority of systems with which we are dealing in quantum statistics are such that the degeneracy, discussed a moment ago, is only apparent inasmuch as the wave function describing a system of identical particles must either be completely symmetrical (bosons), or completely anti-symmetrical (fermions) in all the particles. This means that the only possible wave function of the system, called the *accessible* state by Fowler, will be either

$$\psi_{\text{BE}} = C_{\text{BE}} \sum_P P\psi \quad (9)$$

in the case of Bose-Einstein statistics (bosons) or

$$\psi_{\text{FD}} = C_{\text{FD}} \sum_P (-)^P P\psi \quad (10)$$

in the case of Fermi-Dirac statistics (fermions). In (9) and (10)  $C_{\text{BE}}$  and  $C_{\text{FD}}$  are normalization constants, the sums are over all  $N!$  possible permutations of the  $N$  arguments, and  $(-)^P$  is equal to  $+1$  or  $-1$  according as to whether  $P$  is an even or odd permutation.

We see that the degeneracy has been lifted by the exclusion principle. In fact, in the Fermi-Dirac case (henceforth denoted by FD, just as the Bose-Einstein case will be denoted by BE), some of the states (4) will not even be eigenstates. This will happen as soon as at least one of the  $n_m$  is larger than unity since in that case the interchange of two particles which are in the same one-particle eigenstate will on the one hand leave  $\psi_{\text{FD}}$  unaltered, while according to (10) changing its sign; hence  $\psi_{\text{FD}}$  must vanish in such a case. We get thus the following weights for the BE and the FD case,

$$W_{\text{BE}}(n_m) = 1; \quad (11)$$

$$W_{\text{FD}}(n_m) = 1, \quad \text{if all } n_m \text{ are equal to 0 or 1; } \quad W_{\text{FD}}(n_m) = 0 \text{ otherwise.}$$

Up to now we have made only one assumption, namely, that we are dealing with a system of independent particles. We shall now introduce a second one, namely, that the one-particle energy eigenvalues are lying so densely that we can take large numbers of them together in groups and characterize each group by a relatively well-defined energy value,  $E_j$ . Moreover, we shall assume that not only the number of energy levels  $Z_j$  in the  $j$ th group, but also the number of particles  $N_j$  occupying levels in that group, and if necessary their difference  $Z_j - N_j$ , are sufficiently large numbers so that we may use Stirling's approximation for the factorial,

$$\log x! = x \log x - x, \quad (13)$$

in its crudest form. We do not have the space nor the inclination to discuss in how far this procedure can be justified, but only refer to the next section where we shall show how more rigorous methods lead to the same results as those to be obtained here.

We now first of all evaluate the weight  $W(N_j)$  of a given distribution of the particles over the different groups. Having noted that the  $W(n_m)$  given by (8), (11), and (12) are all products of factors pertaining to single levels, which enables us to split the  $W(N_j)$  into factors each referring to one group only,

$$W(N_j) = \prod_{m,j} W_{m,j}, \quad (14)$$

we then notice that each of the  $W_{m,j}$  is given by the relation

$$W_{m,j} = \sum W_{m,j}(n_m), \quad (15)$$

where the  $W_{m,j}$  contains only those  $n_m$  referring to the  $\epsilon_m$  in the  $j$ th group and where the summation is over all  $n_m$  combinations which add up to  $N_j$ .

In the three cases corresponding to (8), (11), and (12) we get respectively (ESM pp. 74, 75)

$$W_{j,\text{Bo}}(N_j) = \frac{Z_j^{N_j}}{N_j!}, \quad (16a)$$

$$W_{j,\text{BE}}(N_j) = \frac{(N_j + Z_j - 1)!}{N_j! (Z_j - 1)!} \quad (16b)$$

$$W_{j,\text{FD}}(N_j) = \frac{Z_j!}{(Z_j - N_j)! N_j!} \quad (16c)$$

What we have done up to this point is to consider the quantum mechanics of a system of  $N$  independent particles, and we must now introduce a

statistical idea. The main assumption is that *the equilibrium configuration of the system under consideration will be identical with the most probable  $N_i$ -distribution compatible with a given total energy  $E$* . The justification of this assumption has probably never been fully given and a discussion of it leads to extremely complicated and difficult problems. We must therefore refer to the literature<sup>8</sup> (see also ESM, Appendix I) for such a discussion.

In order to find the equilibrium distribution we must find the maximum of the  $W(N_i)$  under the conditions that the total energy of the system is  $E$  and that the total number of particles is  $N$ ,

$$\sum N_i E_i = E \quad (17)$$

$$\sum N_i = N \quad (18)$$

It turns out to be more convenient to determine the maximum of  $\log W(N_i)$  which is given by the equation

$$\log W(N_i) = \sum_i N_i \{ \log [(Z_i + \alpha N_i)/N_i] + (1 - \alpha^2) \} + \alpha Z_i \log [(Z_i + \alpha N_i)/Z_i], \quad (19)$$

where we have combined all three possible cases into one by introducing a parameter  $\alpha$  defined by the equations

$$\alpha_{Bo} = 0, \quad \alpha_{BE} = 1, \quad \alpha_{FD} = -1. \quad (20)$$

The determination of the distribution for which  $\log W$  is maximum while (17) and (18) are satisfied is performed by the method of undetermined multipliers and the result is

$$\log [(Z_i + \alpha N_i)/N_i] = -\nu + \beta E_i, \quad (21)$$

where  $\nu$  and  $\beta$  are Laplacian multipliers, the physical meaning of which will be discussed in a moment.

From (21) we get the following equilibrium distributions

$$N_{Bo} = Z_i \exp(\nu - \beta E_i), \quad (22a)$$

$$N_{BE} = Z_i / [\exp(-\nu + \beta E_i) - 1], \quad (22b)$$

$$N_{FD} = Z_i / [\exp(-\nu + \beta E_i) + 1]. \quad (22c)$$

From (22a) we see that we have obtained for this particular case the so-called Boltzmann distribution; hence the subscript "Bo." We shall denote this case hence forth the Boltzmann, or Bo, case even though it was derived in a quantum mechanical framework rather than a classical one.

We may draw attention to the fact that if  $e^{-\nu} \gg 1$ , so that for all values of  $j$   $N_j \ll Z_1$ , expressions (22b and c) go over into expression (22a). We shall call this the classical limit and we shall discuss in § 1.3 under what circumstances this limit can be taken.

To show the physical meaning of  $\nu$  and  $\beta$  we must consider two systems for which  $\nu$ ,  $\beta$ , and the external parameters  $a_k$  have slightly different values. The external parameters are those variables such as the volume of the system or the strength of an external magnetic or electric field on which the energy levels  $\varepsilon_m$  may depend. By considering two slightly different equilibrium situations we find (ESM § 4.4) that  $\beta$  is related to the absolute temperature  $T$  through the equation ( $k_B$ : Boltzmann's constant)

$$\beta = 1/k_B T, \quad (23)$$

while  $\nu/\beta$  is equal to the partial free energy, or the thermal potential per particle.

Moreover, one can introduce Kramers'  $q$ -potential by the equation

$$q = \log W + \nu N - \beta E = \sum_j N_j (1 - \alpha^2) + \sum_j \alpha Z_j \log \left( \frac{Z_j + \alpha N_j}{Z_j} \right), \quad (24)$$

where we have used (19) and (20), and where the  $N_j$  are given by (22). This  $q$ -potential which through (22) and (24) is a function of  $\nu$ ,  $\beta$ , and of the  $a_k$  entering into the  $E_j$ , determines completely the thermodynamic behaviour of the system and we have, for instance, the relations (for a proof of these equations we refer again to ESM)

$$\beta p V, \quad N = \frac{\partial q}{\partial \nu}, \quad E = - \frac{\partial q}{\partial \beta}, \quad \beta A_k = \frac{\partial q}{\partial a_k}, \quad (25)$$

where  $p$  is the pressure in the system,  $V$  its volume, and  $A_k$  the "generalized force" exerted by the system on the parameter  $a_k$  (see ESM for a discussion),

$$A_k = - \sum_m n_m \frac{\partial \varepsilon_m}{\partial a_k} = - \sum_j N_j \frac{\partial E_j}{\partial a_k} \quad (26)$$

In the case where  $a_k$  is the magnetic field,  $A_k$  is the magnetic moment of the system, while for  $a_k \equiv V$ ,  $A_k = p$ .

## 1.2 The Method of the Quantum Mechanical Grand Canonical Ensembles

Although it is often a surprisingly good approximation to treat real physical systems as systems of independent particles, it is, of course, a fact that real physical systems consist of interacting particles, and it is necessary

to develop methods which are capable of dealing with such systems. One method is that of the grand ensembles introduced by Gibbs in his famous monograph. In the present section we shall develop the method of the quantum mechanical grand (canonical) ensembles. We first of all draw attention to the fact that quantum mechanics by its very nature is statistical in character, and the density matrix formalism which we shall discuss was originally introduced to describe one system, while we shall use it to describe an ensemble of systems, that is, we shall apply it to a case where the statistical aspects inherent in quantum mechanics are joined to the statistical aspects which enter into the statistical mechanical discussion, whether a classical or a quantum mechanical one.

Let us for a moment consider the collective of  $N$  identical systems all governed by the same energy operator  $\mathbf{H}$ . Let  $\Psi^k$  be the wave function describing the  $k$ th system satisfying the equation

$$\mathbf{H}\Psi^k = i\hbar\dot{\Psi}^k. \quad (27)$$

We now introduce a complete orthonormal set  $\phi_n$  (for the sake of simplicity we shall not explicitly introduce degeneracy, continuous eigenspectra, or relativistic effects, so that the  $\Psi^k$  are scalars) and expand  $\Psi^k$  in terms of this set,

$$\Psi^k = \sum a_n^k \phi_n, \quad a_n^k = \int \phi_n^* \Psi^k d\tau. \quad (28)$$

The  $a_n^k$  can, of course, be used to describe the  $k$ th system, and they satisfy the transformed Schrödinger equation

$$i\hbar\dot{a}_n^k = \sum_m H_{nm} a_m^k, \quad H_{nm} = \int \phi_n^* \mathbf{H} \phi_m d\tau. \quad (29)$$

If the  $\Psi^k$  are normalized, we have

$$\sum |a_n^k|^2 = 1. \quad (30)$$

We now introduce a density operator  $\rho$  by defining its matrix elements in our chosen representation,

$$\rho_{mn} = N^{-1} \sum_{k=1}^N a_m^k a_n^{k*}. \quad (31)$$

From (29) and (31) it follows that  $\rho$  satisfies the equation

$$i\hbar\dot{\rho} = [\mathbf{H}, \rho]_-, \quad (32)$$

where  $[\mathbf{A}, \mathbf{B}]_- = \mathbf{AB} - \mathbf{BA}$  is the commutator of  $\mathbf{A}$  and  $\mathbf{B}$ .

If  $G$  is the operator corresponding to some physical quantity, its average value  $\langle G \rangle$  is given by the equation

$$\langle G \rangle = N^{-1} \sum_{k=1}^N \int \Psi^k* G \Psi^k d\tau \quad (33)$$

We note the double average, once over the state  $\Psi^k$ , and once over all  $N$  systems in the ensemble.

From (28), (31), and (33) it follows that we can write  $\langle G \rangle$  in the form

$$\langle G \rangle = \text{Tr}(\rho G), \quad (34)$$

while we also note either by putting  $G = 1$  in (34), or by using (30), that  $\rho$  is normalized, that is,

$$\text{Tr} \rho = 1 \quad (35)$$

In the case of a stationary ensemble,  $\rho$  must commute with  $H$  (see Eq. 32). There are many cases where one would like to consider a system in which reactions can take place (see § 1.3). In that case one must include in the ensemble systems which differ in the number of particles they contain. In that case  $\rho$  must also commute with the number operators  $n_i$  — the Jordan-Klein and Jordan-Wigner matrices

The only kind of density operator we shall consider is the grand canonical one which is given by the equation

$$\rho = \exp \left[ -q + \sum_i n_i \nu_i - \beta H \right]. \quad (36)$$

The  $q$ ,  $\nu_i$ , and  $\beta$  are  $c$  numbers, and  $H$  is the Hamiltonian of a system in which there are  $n_1$  particles of the first kind,  $n_2$  of the second kind, ..., while the  $n_i$  are the number operators. The grand potential  $q$  plays now the same role as Kramers'  $q$ -potential in § 1.1, and it is determined from the normalization condition (35),

$$e^q = \text{Tr} \left[ \exp \left( \sum_i n_i \nu_i - \beta H \right) \right]. \quad (37)$$

As the eigenvalues of the  $n_i$  are the integers  $n_i$ , we can write (37) also in the forms

$$e^q = \prod_i \left| \sum_{n_i=0}^{\infty} \exp(n_i \nu_i) \right| \text{Tr} e^{-\beta H}, \quad (38a)$$

$$= \prod_i \left[ \sum_{n_i=0}^{\infty} \exp(n_i \nu_i) \right] S \exp[-\beta E(n_i; n)], \quad (38b)$$

where  $E(n_i; n)$  indicates the  $n$ th energy level of a system in which there are  $n_1$  particles of the first kind, . . . .

It can be shown (ESM, Chapter VII) that the  $\nu_i/\beta$  are the partial thermal (or chemical) potentials and that  $\beta$  is again given by (23). Once more, we can not discuss the physical reasons for attaching so much importance to grand ensembles (ESM § 6.1), but we may remind the reader of the following theorem: *The macroscopic behaviour of a system of different kinds of particles with partial chemical potentials  $\nu_i/\beta$  at a temperature  $T [= (k_B \beta)^{-1}]$  will be described correctly by taking the average behaviour of a system in a grand canonical ensemble with a density operator given by Eq. (36).* Of the utmost importance is also the fact that one can show that, in general, fluctuations are small, or if not small so fast that their time average is small. As we have no space to discuss fluctuations we shall not make this last statement more rigorous. The macroscopic behaviour of a system is completely determined by the average values of the various physical quantities of interest which are determined by using (34). Many of these can be determined once  $q$  is determined as a function of  $\beta$ , the  $\nu_i$ , and the external parameters  $a_k$  which enter into the Hamiltonian. In particular we find the following equations, which are analogous to Eqs. (25)

$$q = \beta p V, \quad \langle n_i \rangle = \frac{\partial q}{\partial \nu_i}, \quad \langle E \rangle = \frac{1}{\beta} \frac{\partial q}{\partial \beta}, \quad \beta \langle A_k \rangle = \frac{\partial q}{\partial a_k}, \quad (39)$$

In the next section we shall discuss a few applications of the quantum mechanical grand ensembles, but we may perhaps use them at this moment to show how one can derive (22) and (24) of the previous subsection without making any additional assumptions but that we are dealing with a system of independent particles.

If we are dealing with a system of only one kind of particle we can drop the index  $i$  on the  $n_i$  and  $\nu_i$ , and we have as in (17) and (18),

$$n = \sum n_m, \quad E = \sum n_m \epsilon_m, \quad (40)$$

where the  $n_m$  and  $\epsilon_m$  have the same meaning as in the previous subsection. We can use (38b) but must introduce the degeneracy of the energy  $E$  which is given by the  $W(n_m)$  of (8), (11), and (12). For the grand potential we get the three equations

$$\begin{aligned} \epsilon^q &= \sum_{n=0}^{\infty} \sum_{\sum n_m = n} \left[ \prod_m (n_m!)^{-1} \right] \exp \left[ \sum n_m (\nu - \beta \epsilon_m) \right] \\ &= \prod_m \sum_{n_m=0}^{\infty} \exp \left[ \sum n_m (\nu - \beta \epsilon_m) \right] / n_m!, \end{aligned}$$



or

$$q = \sum_m \exp(\nu - \beta \epsilon_m); \quad (41 \text{ Bo})$$

$$\begin{aligned} e^q &= \sum_{n=0}^{\infty} \sum_{\sum n_m = n} \exp \left[ \sum n_m (\nu - \beta \epsilon_m) \right] \\ &= \prod_m \sum_{n_m=0}^{\infty} \exp \left[ \sum n_m (\nu - \beta \epsilon_m) \right] \end{aligned}$$

or

$$q = - \sum_m \log [1 - \exp(\nu - \beta \epsilon_m)]; \quad (41 \text{ BE})$$

$$\begin{aligned} e^q &= \sum_{n=0}^{\infty} \sum_{\sum n_m = n (n_m \leq 1)} \exp \left[ \sum n_m (\nu - \beta \epsilon_m) \right] \\ &= \prod_m \sum_{n_m=0}^1 \exp \left[ \sum n_m (\nu - \beta \epsilon_m) \right], \end{aligned}$$

or

$$q = \sum \log [1 + \exp(\nu - \beta \epsilon_m)]. \quad (41 \text{ FD})$$

Equations (41) are the same as Eqs. (24), with two differences however. First of all we have not made the assumption that the energy levels are lying densely, and secondly we now have a sum over the individual energy levels, and not over groups of energy levels.

To derive (22) we treat the  $\epsilon_m$  as external parameters and use the relation

$$\beta \langle n_m \rangle = \frac{\partial q}{\partial \epsilon_m} \quad (42)$$

### 1.3 Applications

In this subsection we shall discuss two topics. First of all we shall discuss under what circumstances quantum statistics rather than classical statistics should be applied. Secondly we shall show how the method of the grand ensembles can be used to obtain the Saha formula for dissociative equilibria.

We noticed in § 1.1 that classical statistics could be applied provided  $e^{-\nu} \gg 1$ . Let us assume that this condition is satisfied and investigate what this implies for the case of a system of point particles in a volume  $V$ . We use (24) and see that now we have for the  $q$  potential ( $\alpha$  can be put equal to zero if  $e^{-\nu} \gg 1$ )

$$q = \sum N_i = e^{\nu} \sum Z_i \exp(-\beta E_i) = e^{\nu} \int dZ e^{-\beta \epsilon}, \quad (43)$$

where  $dZ$  is the number of levels in the energy interval  $\epsilon, \epsilon + d\epsilon$ . For  $dZ$  we have (ESM, p. 82)

$$dZ = 2\pi \left( \frac{2m}{h^2} \right)^{3/2} V \epsilon^{1/2} d\epsilon, \quad (44)$$

and substituting this into (43) we find for  $q$

$$q = \left( \frac{2\pi m}{\beta h^2} \right)^{3/2} V e^{\nu}, \quad (45)$$

or using the relation  $N = \partial q / \partial \nu = q$

$$e^{-\nu} = \left( \frac{2\pi m}{\beta h^2} \right)^{3/2} \left( \frac{N}{V} \right)^{-1} \quad (46)$$

From (46) we notice first of all that  $e^{-\nu} \rightarrow \infty$  as  $h \rightarrow 0$  as we should have expected. Secondly, we see that  $e^{-\nu} \rightarrow \infty$  as  $\beta \rightarrow 0$  ( $T \rightarrow \infty$ ),  $m \rightarrow \infty$ , or  $N/V \rightarrow 0$ , that is, we may expect classical behaviour at high temperatures, low densities, and for heavy particles. It may be noted that  $e^{-\nu}$  is essentially the ratio of the cube of the de Broglie wavelength of particles of kinetic energy  $\beta^{-1}$  to the specific volume per particle.

To see whether in any particular case  $e^{-\nu}$  is, indeed, large compared with unity let us consider a number of gases at their boiling point. For argon, neon, hydrogen, and the two isotopes of helium we find for  $e^{-\nu}$  respectively the values 500,000, 10,000, 140, 8, and 3. We see that only in the case of hydrogen and helium quantum effects may begin to play a role. Even in those cases, however, classical statistics is a reasonable first approximation. We refer to Chapter VIII of ESM for a discussion of the equation of state of gases.

We see that even at 3.2 °K (the boiling point of He<sup>3</sup>) and a light gas (He<sup>3</sup>) quantum effects will be small. If we are looking for such effects we must either look for cases where the density is much higher, or for the case of electrons. The first case arises, for instance, in the case of liquid helium which will be discussed briefly in § 2.3. Another case of high densities is that of

nuclear matter. Quantum statistics has been used both to give a statistical discussion of nuclear reactions and to discuss nuclear matter at high densities in stellar interiors (ESM, Chapters XIII and XIV). In the case of electrons, their small mass will make  $e^{-}$  small compared with unity, even at relatively high temperatures. The most often considered case is the one of the conduction electrons in a metal for which  $e^{-}$  at room temperature is of the order of  $10^{-5}$ . To conclude this discussion we wish to consider very briefly the case of semiconductors, using a simplified model due to Wilson (ESM, Chapter XI). In this model the conduction electrons at any temperature are produced by their excitation across an energy gap  $\Delta\epsilon$ , and their number will thus increase with increasing temperature. If  $n_0$  is the number of centres which can produce conduction electrons, one finds for the density of the conduction electrons,  $n_c$ , the equation

$$n_c = (2n_0)^{1/2} (2\pi m/\beta h^2)^{3/4} \exp(-\frac{1}{2}\beta\Delta\epsilon), \quad (47)$$

where  $m$  is now the electron mass. Whether or not the conduction electrons can be described by classical statistics depends on whether or not the following inequality is satisfied

$$n_c(2\pi m/\beta h^2)^{3/2} \ll 1, \quad (48)$$

or

$$2n_0(\beta h^2/2\pi m)^{3/2} e^{-\beta\Delta\epsilon} \ll 1. \quad (49)$$

In most cases  $\Delta\epsilon$  is so large and  $n_0$  so small that inequality (49) is always satisfied, leading to the well-known result that semiconductor electrons obey (generally) Boltzmann statistics. However, in some cases  $\Delta\epsilon$  may be so small that the left-hand side of (49) actually becomes larger than unity, for a certain range of temperatures. It is worth noting that both for very high temperatures *and for very low* temperatures condition (49) is satisfied. The necessity to use classical statistics at high temperatures is normal, but the transition from quantum to classical statistics on *lowering* the temperature is at first sight rather surprising; it comes about, of course, because of the exponential factor in expression (47) for  $n_c$ , that is, because of the extreme paucity of conduction electrons at very low temperatures. We may add that although the transition from classical to quantum statistics has been observed in certain semiconductor samples — the only clear case of such a transition — the second transition back to classical statistics has not yet been observed; it must be borne in mind, however, that the extremely simple model on which our considerations have been based are almost certainly inadequate to describe actual semiconductors.

We shall now consider the following equilibrium



which may describe either the formation and dissociation of a diatomic molecule or the recombination of an ion and an electron and the ionization of an atom. We shall simplify the situation for the moment by assuming that our system only contains as its constituents A, B, and AB, although the advantage of the method of the grand ensembles is that one can consider any number of constituents at the same time, and thus discuss easily complicated equilibria, both of many constituents, all mutually reacting, and ionization equilibria where once, twice, thrice, ... ionized atoms occur simultaneously.

Equation (38b) is now of the form

$$e^q = \sum_{n_B} \sum_{n_{AB}} \exp(n_A \nu_A + n_B \nu_B + n_{AB} \nu_{AB}) \\ \mathcal{S} \gamma_k \exp[-\beta E(n_A, n_B, n_{AB}, k)], \quad (51)$$

where we have explicitly introduced the degeneracy  $\gamma_k$  of the level  $E(n_A, n_B, n_{AB}; k)$ . As we are considering the equilibrium (50) the  $\nu$  satisfy the relation

$$\nu_A + \nu_B = \nu_{AB}. \quad (52)$$

We now assume that all particles in the system are independent so that we may write

$$E(n_A, n_B, n_{AB}; k) = E(n_A; k_A) + E(n_B; k_B) + E(n_{AB}, k_{AB}), \quad (53)$$

$$\gamma_k = \gamma_{kA} \gamma_{kB} \gamma_{kAB}, \quad (54)$$

and we get

$$e^q = \sum_{n_A} \exp(n_A \gamma_A) \mathcal{S}_A \gamma_{kA} \exp[-\beta E(n_A; k_A)] \{B\} \{AB\}. \quad (55)$$

As the particles are supposed to be independent we have

$$E(n_A; k_A) = \sum_{mA} n_{mA} \varepsilon_{mA}, \quad \sum n_{mA} = n_A, \quad (56)$$

similarly for A and AB.

Let  $g_{mA}$  be the degeneracy of the particle level  $\varepsilon_{mA}$  and let us assume that we may neglect symmetry effects, so that we get for  $\gamma_{kA}$  the expression (cf. Eq. 8)

$$\gamma_{kA} = \prod_{mA} \frac{g_{mA}^{n_{mA}}}{n_{mA}!} \quad (57)$$

Evaluating the right-hand side of Eq. (55) we get

$$q = Sg_{mA} \exp(\nu_A - \beta\varepsilon_{mA}) + S(B) + S(AB). \quad (58)$$

This result is hardly surprising, giving us  $q$  — which is proportional to the pressure — as the sum of the partition functions (as the sums in (58) are called) pertaining to the three different constituents.

The energies  $\varepsilon_{mA}$ , ... consist of two parts, the kinetic energy corresponding to the motion of the centre of gravity of the particles, and the internal energy, i.e., the atomic energy levels in the case of atoms and the electronic vibrational and rotational energy in the case of molecules. As far as the kinetic energy is concerned, a summation over all possible kinetic energy levels will lead to a factor  $(2\pi m/\beta h^2)^{3/2} V$  (see the beginning of this subsection), where  $m$  is the mass of the particle concerned and  $V$  the volume of the system.

Usually partition functions are evaluated, reckoning all energies from the ground state as zero. If we do that we shall prime the energies. If  $D$  is the dissociation energy of the reaction (50) we can fix the zero of the unprimed energies in such a way that

$$\varepsilon_{kinA} + \varepsilon'_{mA} = \varepsilon_{mA}, \quad \varepsilon_{kinB} + \varepsilon'_{mB} = \varepsilon_{mB}, \quad \varepsilon_{kinAB} + \varepsilon'_{mAB} = \varepsilon_{mAB} + D. \quad (59)$$

Using (39) and introducing the concentrations  $c_i = n_i/V$  we find easily

$$\left( \frac{c_A c_B}{c_{AB}} \right) = \left( \frac{2\pi\mu}{\beta h^2} \right)^{3/2} e^{-\beta D} \left[ \sum_{\varepsilon_{mA}} \exp(-\beta\varepsilon'_{mA}) \right] \left[ \sum (B) \right] \left[ \sum (AB) \right]^{-1}, \quad (60)$$

where  $\mu$  is the reduced mass  $(= m_A m_B / m_{AB})$ .

In the case of a dissociation equilibrium we may to a first approximation write

$$\begin{aligned} \varepsilon'_{mAB} &= \varepsilon'_{el} + \varepsilon'_{rot} + \varepsilon'_{vib}, \\ \varepsilon'_{rot} &= \frac{j(j+1)h^2}{8\pi^2} I, \quad g_j = 2j+1, \quad j = 0, 1, 2, \dots, \\ \varepsilon'_{vib} &= v h \omega, \quad g_v = 1, \quad v = 0, 1, 2, \dots, \end{aligned} \quad (61)$$

where  $I$  is the moment of inertia of the molecule AB and  $\omega$  the vibrational frequency. Assuming that we may replace the sums over  $\varepsilon'_{mA}$ ,  $\varepsilon'_{mB}$  and  $\varepsilon'_{el}$

by their first term, putting the corresponding degrees of degeneracy equal to  $g_A$ ,  $g_B$ , and  $g_{AB}$ , and assuming that we may replace the sum over  $j$  by an integral, we find finally

$$\frac{c_A c_B}{c_{AB}} = \left( \frac{g_A g_B}{g_{AB}} \right) \left( \frac{2\pi\mu}{\beta h^2} \right)^{3/2} \left( \frac{\beta h^2}{8\pi^2} I \right) e^{-\beta D} (1 - e^{-\beta h\omega}), \quad (62)$$

which is the usual form of the Saha formula for a dissociative equilibrium. Equation (60) can also easily be applied to the case of an ionization equilibrium.

Klein and collaborators have used the method of the quantum mechanical grand ensembles to discuss a system of nuclear species at high pressures and temperatures; this system was supposed to represent the primordial material from which the chemical elements in their present abundances were produced in a statistical equilibrium. The system considered by Klein contained not only all possible nuclear species, but also electrons, positrons, photons, and neutrinos. We refer to Chapter XIV of ESM for a discussion of this theory and further references.

## 2. Systems of Bosons

In the limited space of one chapter we must restrict the discussion, and the rest of this chapter will be devoted to systems of either bosons, or fermions. In § 2 we shall discuss systems of bosons, first of all in § 2.1 a perfect BE gas and its condensation and secondly in § 2.2 the BE gas of hard spheres which has recently been the subject of a number of papers by Yang, Lee, Huang, Dyson, Brueckner, and others. In § 2.3 we shall briefly discuss liquid helium.

### 2.1 The Perfect BE Gas

In § 1 we derived all formulas necessary to discuss a perfect BE gas. They are Eqs. (39), (41 BE), and (44). As long as  $e^\nu$  is smaller than unity we can expand the logarithm and we get

$$\begin{aligned} q &= -2\pi \left( \frac{2m}{h^2} \right)^{3/2} V \int_0^\infty \epsilon^{1/2} \log(1 - e^{\nu - \beta\epsilon}) d\epsilon \\ &= 2\pi \left( \frac{2m}{h^2} \right)^{3/2} V \sum_{n=1}^\infty n^{-1} \int_0^\infty x^{1/2} e^{(n\nu - nx)} dx \\ &= \left( \frac{V}{\lambda^3} \right) f(y), \end{aligned} \quad (63)$$

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where  $v_0$  is essentially the cube of the de Broglie wavelength of a particle with kinetic energy  $\beta^{-1}$ ,

$$v_0 = \left( \frac{\beta \hbar^2}{2\pi m} \right)^{3/2} \quad (64)$$

where  $y$  is the absolute activity,

$$y = e^{\nu}, \quad (65)$$

and where  $f(y)$  is given by the equation

$$f(y) = \sum_{n=1}^{\infty} \left( \frac{y^n}{n^{5/2}} \right). \quad (66)$$

The variable  $y$  is a function of the specific volume  $v(= V/N)$  through the relation

$$N = \frac{\partial q}{\partial v} = \frac{y}{\partial y} \frac{\partial q}{\partial y} = \left( \frac{V}{v_0} \right) y f'(y). \quad (67)$$

As  $q = \beta p V$ , Eqs. (63) and (67) together give us  $p$  as a function of  $\beta$  and  $V$ . This will give us the equation of state as long as the power series for  $f(y)$  and  $f'(y)$  converge. This is the case as long as  $y \leq 1$ , or, as long as  $v$  is larger than a critical value  $v_c$  given by the equation

$$v_c = \frac{v_0}{f'(1)}, \quad f'(1) = \sum_{n=1}^{\infty} n^{-3/2} = \zeta\left(\frac{3}{2}\right) = 2.61, \quad (68)$$

where  $\zeta(n)$  is Riemann's zeta function.

The next question is: What will happen if we reduce, at constant temperature, the volume  $V$  below the value  $Nv_c$ ? This question was considered by Einstein in 1925, and he argued that as the expression (67) for the specific volume can never be smaller than  $v_0/f'(1)$ , on decreasing the volume  $V$  to a value  $V_1$ , say, which is less than  $Nv_c$ , a fraction  $(Nv_c - V_1)/Nv_c$  of the particles will "condense," that is, drop out of the system, and a fraction  $V_1/Nv_c$  will constitute the gaseous phase. The condensation will take place into the lowest available particle level and the condensed particles will not contribute to the pressure, leading to a horizontal branch of the isotherm, just as in the case of ordinary condensation of a liquid. In recent years this phenomenon of the Einstein condensation has attracted a lot of attention because of a possible application to the lambda-transition of liquid helium to be discussed in § 2.3. We shall therefore discuss it in somewhat more detail, and see that, indeed, Einstein's predictions are fully borne out by a more rigorous analysis.

From (67) and (68) it follows that as  $v$  approaches  $v_c$ ,  $\nu$  will approach the value zero. In that case the replacement of the sum in (41 BE) by an integral is no longer safe, and it is advisable to consider the original sum, so that we have, instead of Eq. (67),

$$N = \sum [\exp(-\nu + \beta \varepsilon_m) - 1]^{-1} \left( = \sum n_m \right), \quad (69)$$

where in writing down the last equality we have used Eq. (22b) in the form (42). The only term from which we may expect trouble is the one corresponding to the ground state  $\varepsilon_0 (= 0)$ . If we split that term off, we can replace the remaining sum by an integral, and the result is

$$N = n_0 + (V/v_0) y f'(y), \quad (70)$$

where  $n_0$  is given by the equation

$$n_0 = (e^{-\nu} - 1)^{-1}. \quad (71)$$

Equation (70) can be rewritten in the form

$$1 = \frac{n_0}{N} + \frac{v y f'(y)}{v_c f'(1)}. \quad (72)$$

This last equation is valid for all values of  $v$ . The first term on its right-hand side gives us the fraction of the particles which are in the ground state. If  $v < v_c$ , we would expect  $\nu$  to be essentially equal to zero, or  $y \doteq 1$ , and we see that, indeed, a fraction  $1 - (v/v_c)$  of the particles is condensed into the ground state. For  $y \doteq 1$  Eq. (71) takes the form

$$n_0 \doteq (1 - y)^{-1}, \quad (73)$$

and we find from Eq. (72)

$$y \doteq 1 - \frac{v_c}{N(v_c - v)}, \quad (v < v_c) \quad (74)$$

which shows that our expectation to find  $y \doteq 1$  was correct, the correction term being only of the order  $N^{-1}$ , that is, totally negligible. As  $y$  is essentially constant for  $v < v_c$ ,  $q$  will also be constant, and so will  $p$ . In the case of  $q$ , the term corresponding to the ground state will only make a negligible contribution, in contradistinction to its non-negligible contribution in the case of  $K$ . ~~the reason is that the pressure exerted by a particle is proportional to its energy, so that the pressure exerted by the particles in the ground state will be  $n_0 \varepsilon_0 (= 0)$ .~~

So far we have considered what could happen if at constant temperature the volume is decreased. We can also consider what would happen when at



constant  $v$  the temperature is decreased. Condensation will again set in, at a temperature  $T_c$  given by the equation (cf. Eqs. 68 and 64)

$$T_c = \left( \frac{h^2}{2\pi m k_B} \right) [f'(1)v]^{-2/3} = 120 \rho^{2/3} M^{-5/3} \text{ } ^\circ\text{K}, \quad (75)$$

where  $M$  is the molecular weight of the gas, and  $\rho$  its density in  $\text{gm cm}^{-3}$ .

The pressure as a function of temperature follows from the equation  $q = \beta p V$ , and we have

$$\begin{aligned} p &= \left( \frac{2\pi m k_B}{h^2} \right)^{3/2} k_B T^{5/2} f(y), & T > T_c; \\ p &= \left( \frac{2\pi m k_B}{h^2} \right)^{3/2} k_B T f(1), & T < T_c; \end{aligned} \quad (76)$$

where  $y$  (for  $T > T_c$ ) is still a function of  $T$  through Eq. (67).

The specific heat per particle  $c_v$  follows from the energy  $\langle E \rangle$  through the relation

$$c_v = N^{-1} \frac{d\langle E \rangle}{dT}, \quad (77)$$

while from (39) and (63) it follows that

$$3pV = 2\langle E \rangle \quad (78)$$

It may be noted here that (78) is a direct consequence of the fact that the energy levels  $\epsilon_m$  are proportional to  $V^{-2/3}$  (ESM, p. 86) and it holds therefore independent of the statistics of the particles.

From (77) and (78) we get the specific heat per particle. Below  $T_c$  we get simply

$$c_v = \left[ \frac{15k_B v f(1)}{4} \right] \left( \frac{2\pi m k_B}{h^2} \right)^{3/2} T^{3/2}, \quad T \leq T_c. \quad (79)$$

while for  $T > T_c$  we must take into account the fact that  $y$  depends on  $T$ . At  $T_c$ ,  $c_v$  is equal to  $1.9 k_B$ ; it is a continuous function of  $T$ , but  $dc_v/dT$  has a discontinuity at  $T_c$ .

The number of particles in the ground state follows from (68), (64), and (75), and we have

$$\frac{n_0}{N} = 1 - \left( \frac{T}{T_c} \right)^{3/2}, \quad T < T_c. \quad (80)$$

## 2.2 The BE Gas of Hard Spheres

We have mentioned several times that one of the reasons why various authors have studied BE systems has been the interest in the curious behaviour of liquid helium. As two helium atoms interact, albeit weakly, a better approximation to the helium system would be a BE system of weakly interacting particles. Since the helium-helium interaction potential has only a very weak attractive part, it seems a very fair approximation to consider the helium atoms to be hard spheres. Such a BE system of hard spheres has been studied recently by many authors, but we shall only briefly refer to some of their results, obtained by Huang *et al.*<sup>9</sup> Many of their results we shall quote without proof and we must refer to the original papers for all details.

As long as it is possible to consider our system at a density which is sufficiently low, we can treat the interactions between the particles as perturbations. Quantitatively this means for the case of a hard sphere gas that we shall express various quantities in power series in the particle radius  $a$ . The quantities of interest to us are the energy levels, since once they are known we can use (38b) to obtain the grand potential and, hence, all thermodynamic properties of our system. The energy levels in zeroth approximation will be given by (40), and in first approximation we have<sup>9</sup>

$$E_k = \sum_m n_m \varepsilon_m + \frac{ah^2}{\pi m V} \left( N^2 - \frac{1}{2} \sum_m n_m^2 \right), \quad (81)$$

where the  $\varepsilon_m$  are the single particle energy levels,

$$\varepsilon_m = \frac{h^2 k_m^2}{2m}, \quad (82)$$

where  $\mathbf{k}_m$  is the wave vector corresponding to  $\varepsilon_m$ .

Equation (81) is interesting for a number of properties. First of all we note that the first order correction to the energy levels consists of two terms: the first one is positive and proportional to  $N^2/V$ , while the second one is negative and is quantum mechanical in nature. The first contribution arises as follows. Each particle moves through a field produced by the other  $N - 1$  particles. Averaged over the whole volume one would expect a more or less constant repulsive potential, the strength of which would be proportional to  $a$ , to  $N$ , and inversely proportional to  $V$ . For the total system of  $N$  particles we would thus expect an increment proportional to  $aN^2/V$ . The second, negative, contribution is such that the energy will be lowest when all particles are in the same state, i.e., have the same momentum. (The

expression  $\Sigma n_m^2$  is largest for given  $\Sigma n_m = N$  if one of the  $n_m$  is equal to  $N$  and the others equal to zero.) This is a consequence of the quantum mechanical theorem that *for a BE system spatial repulsion leads to momentum-space condensation*. This theorem follows from the Heisenberg principle when applied to  $x_1 - x_2$  and  $p_1 - p_2$ , where  $x_1$ ,  $x_2$ , and  $p_1$ ,  $p_2$  are respectively the coordinates and momenta of two interacting particles. As for a BE system the wave function must be symmetrical in  $x_1$  and  $x_2$ , it follows that  $\Delta(x_1 - x_2)$  will tend to increase if there are repulsive forces, and if  $\Delta(x_1 - x_2) \cdot \Delta(p_1 - p_2)$  remains constant  $\Delta(p_1 - p_2)$  must decrease. We must draw attention to the fact that one should not emphasize too strongly the term condensation in momentum space as if this were something completely different from ordinary condensation. This is not the case as can easily be seen if we remind ourselves that ordinary condensation is essentially the process whereby particles leave the gas phase and do no longer contribute to the gas pressure which is due to the random kinetic motion of the particles. In the case of condensation in momentum space the particles will also leave the "phase" of random motion and enter a "phase" of organized motion. In the case of the perfect BE gas, for instance, the "condensed" phase is that of the particles in the ground state which as we noticed in § 2.1 will, indeed, not contribute to the pressure.

A second point to notice about the energy levels (81) is that the energy spectrum which in its unperturbed form was a highly degenerate continuum is now a collection of degenerate continua which are displaced by a finite amount with respect to one another, each continuum is characterized by a different value of the number of particles in the particle lowest level in the unperturbed state. (In the perturbed system it has no longer sense to talk about particle levels.) The distance  $\Delta$  of the bottom of one continuum to the bottom of the next one is found from (81) to be given by the equation

$$= \left( \frac{a\hbar^2}{\pi m} \right) \left( \frac{n_0}{V} \right). \quad (83)$$

It has not been possible, as yet, to evaluate exactly the equation of state of the hard sphere gas. However, Huang, Yang, and Luttinger considered a system of which the energy levels were given by the following expression,

$$E_k = \sum_m n_m \varepsilon_m + \left( \frac{a\hbar^2}{\pi m V} \right) \left( N^2 - \frac{1}{2} n_0^2 \right). \quad (84)$$

This should, in the region where the system shows a phase transition ("condensation"), be a reasonable approximation to expression (81) since in that

region  $n_0$  will be much larger than any of the other  $n_m$ . We should thus expect that the fictitious system, the energy levels of which are given exactly by expression (84), should for many purposes be a reasonable approximation to the hard sphere BE gas, or even to helium.

The energy levels (84) must now be substituted into (38b). The sum over all possible total numbers of particles can now be split, as was done in evaluating expression (41 BE), into sums over  $n_m$ . These sums are the same as in the case of (41 BE) for all  $n_m$  except  $n_0$ , and their evaluation is therefore straightforward. To evaluate the sum over  $n_0$  one uses the method of steepest descents (ESM, p. 440; see also ESM, Appendix IV) and the final result is that the equation of state is given by the equations

$$p = \left( \frac{2\pi m k_B}{h^2} \right)^{3/2} k_B T^{5/2} f(y) + 2a k_B T v_0^{2/3} \left( \frac{N}{V} \right)^2 - \left( \frac{k_B T}{4a v_0^{2/3}} \right) (\log y) \quad (85)$$

$$N = \frac{V}{2a v_0^{2/3}} y f'(y) \log y.$$

( $f(y)$  is defined by Eq. 66). For a discussion of these equations, which strongly resemble Eqs. (76) and (67), we refer to Huang, Yang, and Luttinger's paper. The following is the result of this discussion. If we plot the isotherms of this system we find that at small densities ( $y \ll 1$ ) the isotherms behave like those of the perfect BE gas. At a certain density  $N/V_1$ , say, the system breaks into two phases, and the pressure stays constant until a density  $N/V_2$  is reached. Below that density the system is again in a single phase and the pressure increases with increasing density. The value  $N/V_1$  is less than  $1/v_c$  for the corresponding perfect gas.

There are a number of points on which this transition differs from the one of a perfect BE gas. The most important one is probably that the fictitious system shows a genuine first order, two-phase transition. Secondly, on reaching the totally condensed state, the pressure reassumes its increase, instead of staying constant. This corresponds to the third difference, namely, that the condensed phase contains particles other than those in the ground state.

### 2.3 Liquid Helium

We mentioned earlier that BE systems have often been studied because of their possible resemblance to liquid helium. If we insert into Eq. (75)  $\rho = 0.15 \text{ gm cm}^{-3}$ ,  $M = 4$ , which are the density of liquid helium and its molecular weight, we find  $T_c = 3.2^\circ \text{K}$  which is of the same order of magnitude as the  $\lambda$ -point temperature of  $2.2^\circ \text{K}$ . To treat liquid helium as

a perfect BE gas encounters, however, the following difficulties. (1) The peak in the specific heat of a perfect BE gas is about  $2k_B$  per particle as against the observed peak of about  $12k_B$ . (2) The specific heat of liquid helium seems to be discontinuous at the  $\lambda$ -point. (3) Below the  $\lambda$ -point the specific heat behaves as  $T^6$  or  $T^7$ , and not as  $T^{3/2}$  like the specific heat of a perfect BE gas. (At temperatures below  $0.6^\circ\text{K}$  the specific heat of liquid helium behaves as  $T^3$ .)

Let us now consider in how far the hard sphere BE gas might resemble liquid helium. First of all we must emphasize that it should be a reasonable approximation as the interatomic forces in helium are relatively well represented by a hard sphere potential. The questions now are whether or not it shows a  $\lambda$ -transition, whether it shows the correct temperature dependence of the specific heat at low temperatures, and whether it shows the superfluid properties which are so characteristic of liquid helium below the  $\lambda$ -point.

The first question has *not* been answered. We must emphasize, and it cannot be emphasized too strongly and too often, that if one considers what happens on decreasing the volume starting from a dilute gas, the first transition to be encountered should be the ordinary gas-liquid condensation, and the phase transition considered in the previous subsection is, in our opinion, nothing but this ordinary phase transition. In order to find the  $\lambda$ -transition one should investigate the behaviour for volumes smaller than  $V_2$ . It is doubtful, however, whether this would be sufficient and whether one should not consider the system in a  $p, T$  diagram at a constant volume, rather than in a  $p, V$  diagram at constant temperature.

The second question seems to be answered in the affirmative. From Feynman's work<sup>10</sup> we know that the low-lying states of liquid helium correspond to phonons, i.e., to longitudinal density waves, with wave functions of the kind

$$\psi_{\mathbf{q}} = \sum \exp [i(\mathbf{q} \cdot \mathbf{x}_i)] \psi_0, \quad (86)$$

where  $\mathbf{q}$  is the phonon wave vector and  $\psi_0$  the ground state wave function. Wave functions of the form (86) will lead to an energy spectrum which predicts the proper temperature dependence of the specific heat. Lee, Huang, and Yang have found that, indeed, the wave functions of the low-lying states of the hard sphere BE gas are of the form (86).

As systems of phonons are of interest not only for the low temperature behaviour of liquid helium, but also for the lattice specific heat of solids, we shall briefly show how such a system leads to a  $T^3$  dependence of the specific heat at low temperatures. We are still dealing with a BE system,

but its constituents are now "quasi particles," namely, the phonons, i.e., particles with zero rest mass. Moreover, their total number is not conserved which means that we can use (41 BE) but with  $\nu = 0$ . In the case where the particle mass is equal to zero, we have instead of (44) the following expression for the number of energy levels between  $\varepsilon$  and  $\varepsilon + d\varepsilon$  (cf. ESM, p. 427)

$$dZ = CV\varepsilon^2 d\varepsilon, \quad (87)$$

where  $C$  is a constant depending on the velocity of propagation of the "quasi particles." From Eqs. (41 BE) and (39) we get for the total energy of the system

$$Z = CV \int_0^{\varepsilon_0} \frac{\varepsilon^3}{e^{\beta\varepsilon} - 1} d\varepsilon, \quad (88)$$

where we have put a finite upper limit  $\varepsilon_0$  corresponding to the fact that the total number of phonon degrees of freedom, which is proportional to  $\int_0^{\varepsilon_0} dZ$ , is finite. Introducing a new variable of integration  $x = \beta\varepsilon$  we get

$$Ck_B^4 T^4 V \int_0^{x_0} \frac{x^3}{e^x - 1} dx, \quad x_0 = \beta\varepsilon_0. \quad (89)$$

At low temperatures we may replace the upper limit by  $\infty$ , and find thus the total energy proportional to  $T^4$ , and hence a  $T^3$  dependence for the specific heat.

The same calculations apply, of course, to the case of light quanta, where now at any temperature  $x_0 = \infty$ , so that the  $T^4$ -dependence is true generally, which in this case is the well-known Stefan-Boltzmann law for black body radiation.

The third question can also be answered in the affirmative. Superfluidity follows from a scarcity of energy levels near the ground state,<sup>10</sup> and as we saw in § 2.2 such a scarcity is built into our chosen energy levels. Put differently, we can say that the energy levels (81) or (84) show the energy gap  $\Delta$  which is essential for the two-fluid model of Tisza and F. London which has been so successful in describing the macroscopic behaviour of helium.<sup>11</sup>

### 3. Systems of Fermions

In the last section of this chapter we shall discuss FD systems. In § 3.1 we shall consider a perfect FD gas which to a first approximation gives us

a model of the conduction electrons in a metal. In § 3.2 we shall show how one can use the results for a perfect FD gas to describe statistically the electron cloud surrounding the atomic nucleus.

### 3.1 The Perfect FD Gas

We can now use (39), (41 FD) and (44). The resultant general equations can be found in § 4.7 of ESM. They are not of great interest. Of interest is, however, the case of a so-called *degenerate* FD gas which is realized when  $e^{\nu} \gg 1$ . To discuss that case, which as we discussed in § 1.3 is realized for the case of metals, for instance, we first consider the behaviour of a perfect FD gas at absolute zero. In the BE case all particles were in the lowest state at absolute zero, but that can, of course, not happen in the FD case because of the exclusion principle. The ground state of the system will be the one where the lowest particle energy levels are filled up until all  $N$  particles are accommodated. We can also see this from our equations. Let  $f(\epsilon) d\epsilon$  be the number of particles with energies between  $\epsilon$  and  $\epsilon + d\epsilon$ , which will be given by the equation

$$f(\epsilon) d\epsilon = \frac{1}{e^{-\nu + \beta\epsilon} + 1} dZ = \frac{4\pi V (2m/\hbar^2)^{3/2}}{e^{-\nu + \beta\epsilon} + 1} \sqrt{\epsilon} d\epsilon, \quad (90)$$

(compare Eq. 22c) where we have multiplied  $dZ$  by 2 to take into account the fact that FD particles will have spin which we have assumed to be equal to  $\frac{1}{2}$ . We shall use the fact that the partial thermal potential  $g = \nu/\beta$  will tend to a finite value  $g_0$  as  $\beta \rightarrow \infty$ , or  $T \rightarrow 0$ . We see then that as  $T \rightarrow 0$ ,  $f(\epsilon)$  will tend to the following function

$$T = 0: f(\epsilon) = 4\pi V \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon}, \quad \epsilon < g_0; \quad f(\epsilon) = 0, \quad \epsilon > g_0. \quad (91)$$

The value of  $g_0$  is determined by the equation

$$N = \int_0^{\infty} f(\epsilon) d\epsilon = \int_0^{g_0} 4\pi V \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon} d\epsilon = \left( \frac{8\pi V}{3} \right) \left( \frac{2m}{\hbar^2} \right)^{3/2} g_0^{3/2}. \quad (92)$$

The zero-point energy  $E_0$  is given by the equation

$$E = -\frac{\partial q}{\partial \beta} = 4\pi V \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^{g_0} \frac{\epsilon^{3/2}}{e^{-\nu + \beta\epsilon} + 1} d\epsilon, \quad (93)$$

or,

$$= \left( \frac{8\pi V}{5} \right) \left( \frac{2m}{h^2} \right)^3 g_0^{5/2}, \quad (94)$$

while the zero-point pressure  $p_0$  follows from the relation  $3pV = 2E$  (Eq. 78). Inserting numerical values for an electron gas of density  $10^{24} \text{ cm}^{-3}$  we find  $p_0 \sim 10^6 \text{ atm}$ !

We mentioned in § 1.3 that even at room temperatures one would expect  $e^*$  for the gas of the conduction electrons in a metal to be large compared with unity. We are thus dealing with a degenerate gas at finite temperatures. In order to get expressions for that case we use a theorem of Sommerfeld's (ESM, p. 238) which states that

$$\int g(\epsilon) f(\epsilon) d\epsilon \doteq \int_0^{\epsilon_0} g(\epsilon) d\epsilon + \left( \frac{\pi^2}{6\beta^2} \right) \left( \frac{\partial g}{\partial \epsilon} \right)_{\epsilon = g_0} \quad (95)$$

If we use this relation we find for the energy of the system

$$E \doteq E_0 \left( 1 + \frac{5\pi^2}{12\beta^2 g_0^2} \right). \quad (96)$$

and for the specific heat

$$c_v = N^{-1} \frac{\partial E}{\partial T} = \pi^2 \frac{k_B^2 T}{g_0}. \quad (97)$$

which is the well-known linear specific heat term of the conduction electrons. It must be noted that it is smaller than the classical expression (including a factor 2 for spin)  $3k_B$  by a factor  $\pi^2 k_B T / 3g_0$  which, according to our assumption of degeneracy, is small compared with unity.

### 3.2 The Statistical Theory of the Atom

Although the number of electrons in an atom does not seem to be large enough to enable us to use statistical methods, it is by far too large to allow exact solutions of the equations of motion. One solution is to use the method of self-consistent fields (Chapter 1, § 13.3, in this volume), but the set of equations one is left with is extremely cumbersome and Thomas and Fermi suggested to use statistical methods as follows. Consider a spherically symmetric atom corresponding to a potential energy field  $U(r)$ . Assume now that we can divide the space occupied by the atom into cells such that (1) each cell contains a large number of electrons, and (2)  $U(r)$  changes only very slowly in each cell. In that case we can apply FD statistics to the



electrons in each cell, and one can convince oneself that one must apply the formulas of a degenerate FD system.

Let  $n(\mathbf{x})$  be the electron density. The total kinetic energy  $T$  of the system is given by the equation (cf. Eqs. 92 and 93)

$$T = c_1 \sum n^{5/3} v, \quad (98)$$

where the summation is over all the cells, where  $v$  is the cell volume, and where  $c_1$  is a constant. The potential energy consists of two parts, firstly a term  $U_e$  which is the interelectronic potential energy,

$$U_e = \frac{1}{2} e^2 \int \frac{n(\mathbf{x})n(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d^3\mathbf{x} d^3\mathbf{y}, \quad (99)$$

and secondly a term  $U_n(\mathbf{x})$  which is the potential energy of the electrons in the electric field of the nucleus  $u(\mathbf{x})$ ,

$$U_n = -e \int u(\mathbf{x})n(\mathbf{x}) d^3\mathbf{x}. \quad (100)$$

The total energy  $E$  of the system of electrons is given by the sum of  $T$ ,  $U_e$ , and  $U_n$ , and we require that  $E$  be a minimum for a given total number of electrons  $N$ ,

$$N = \int n(\mathbf{x}) d^3\mathbf{x}, \quad (101)$$

This leads to the following relation for  $n$ ,

$$n = c_2 (U - U_0)^{3/2}, \quad (102)$$

where  $c_2$  and  $U_0$  are constants, and where  $U$  is the total field in which the electrons are moving which is given by the equation

$$U = u(\mathbf{x}) - e \int \frac{n(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d^3\mathbf{y}. \quad (103)$$

Poisson's equation

$$\nabla^2 (U - U_0) = 4\pi n e \quad (104)$$

gives us a second relation between  $U$  and  $n$ . Eliminating  $n$  we get for  $U$  the following differential equation,

$$\nabla^2 (U - U_0) = 4\pi c_2 e (U - U_0)^{3/2}, \quad (105)$$

which is the basic equation of the Thomas-Fermi theory.

We shall not discuss here the solution of this equation, any of its applications, or any of the many improvements made by Gombás and his group, March and others. We refer to recent survey papers by Gombás<sup>12</sup> and March<sup>13</sup> for such details.

*Note added in proof:* There have been a number of important developments since this chapter was written. We wish to mention three.

(a) Huang<sup>14</sup> has further developed the theory of a hard-sphere boson gas and now, indeed, claims to have found two transitions: the  $\lambda$ -transition and the ordinary gas-liquid transition.

(b) Brueckner and Sawada<sup>15</sup> have used the methods employed in the theory of nuclear matter (see Chapter 5 of Volume III) to consider liquid helium with a fair modicum of success

(c) The density matrix has been increasingly applied to various physical situations. Attention is drawn to review articles by Fano,<sup>16</sup> by Husimi, Kitano, and Mishiyama<sup>17</sup> and by the present author<sup>18</sup> for a discussion of this work, as well as for a discussion of modern methods of evaluating the equilibrium density matrix and for extensive lists of references.

## 6. Theory of Solids\*

R. M. Thomson

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The field of solid state physics, from the point of view of quantum mechanics, is an applied field. We do not look for new ways of extending the basic concepts of quantum mechanics. On the contrary, the present

\* As general references for the material in this chapter, see R. Peierls, "Theory of Solids." Oxford Univ. Press, London and New York, 1956, or the somewhat older but more extensive book of F. Seitz, "Modern Theory of Solids." McGraw-Hill, New York, 1938. The various volumes of "Solid State Physics," edited by F. Seitz and D. Turnbull, Academic Press, New York, provide a modern and complete set of reviews on all aspects of the theory of solids.

formulation of the bases of quantum theory is considered to be adequate for the description of matter in the solid state. Also, in only a few problems is it convenient to use the newer quantum field theoretic techniques, and we shall use the simple Schrödinger equation for our discussion. There is one area where it is sometimes convenient to go over to second quantization in the discussion of solids, and that is when electron-lattice interactions are discussed. In that case, the lattice vibrations can be quantized as a set of boson particles obeying the field equation of a harmonic oscillator. A discussion of either superconductivity or of the polaron almost requires the use of field theory methods. However, we shall keep our discussion in this chapter traditional, since we shall want to focus our attention rather on the more basic results of the application of quantum theory to solid bodies.

The quantum mechanical problem of a solid can be stated very simply, but not very meaningfully, by saying that it is the problem of a large number of identical atoms arrayed on a perfectly regular lattice structure. We can even write down the complete Schrödinger equation for this system, but this statement of the problem is not very cogent since the Schrödinger equation which we write down in this way is completely insoluble. It is insoluble in a much more serious way than the many electron atom, and the subject of solid state physics is a study of how to break down the Schrödinger equation into pieces which are tractable. In this field, we build models almost *ad nauseum*, each model containing carefully weighed approximations which are thought to represent the essential features of a property under study without too many extraneous side issues being involved.

We shall need early in our discussion the concept of a band of energy levels for the valence electrons, and in fact, most of the chapter will be devoted to a discussion of it. As a working definition until we get a chance to go into more thorough detail, we can say the following. At infinite separation,  $N$  atoms, considered as a single system, have the same energy level scheme as a single atom, except the degeneracy of each level is multiplied by  $N$ . (See Fig. 1, page 357). As the atoms are brought together into a crystal with finite lattice constant, the degeneracy of the levels is lifted due to the perturbations of the atoms on one another. The splitting is gradual and each level of the isolated atom becomes a spread out "band" of levels in the solid. The band is a nearly continuous spectrum because of the extremely large number of atoms in any macroscopic sample of the solid.

The primary assumption which is nearly always made is to break up the problem of the solid into three slightly overlapping parts: (1) the valence electrons in the valence band, (2) the atomic or ionic cores and (3), the other bands. We could add a fourth category, imperfections,

which we shall discuss briefly at the end of the chapter. Our chapter is broken up into sections which reflect this division. We first discuss an analogy between the valence electron band and free particles in a box. We then develop the main thesis that the Schrödinger equation of the solid can be separated into the three parts already described, and treat the valence electron problem in detail. After a discussion of lattice vibrations as one of the basic parts of the solid synthesis, we then take up the problem of the existence of interactions between the lattice vibrations and the valence electrons. Finally, the problem of imperfections in crystals is treated briefly.

We shall not talk too much about wave functions which are a mixture of more than one band and their effect on the properties of the valence electrons, but shall generally keep our bands autonomous. There are many problems where this is not a feasible assumption, but in an elementary discussion it only adds complication without additional insight. The reason why the division of the system into valence electrons and core ions is possible is the theorem of Born and Oppenheimer, which is discussed in the chapter on molecules. The theorem is as important for our discussion as it is for the discussion of molecules, and for the same reasons. The separation is valid when the core ions and atoms are heavy compared with the electrons, and when the system is in a steady state. In the separation process, the electronic wave functions of the valence electrons follow the core motion in an adiabatic way, and one can in principle find the "Morse function" for the solid just as for the molecule.

Some of the most important phenomena in the theory of the solid state concern the interactions between the valence electrons in the valence band and the motion of the core ions. Examples are the electrical resistance of a metal, superconductivity, and the polaron. (*Polaron* is the name given to an electron excited into the conduction band of an ionic crystal. We might mention that in an ionic insulator crystal like NaCl, the interaction of an electron in the conduction band with the lattice vibrations is *not* small as it is in other cases.) In § 6 we shall discuss the electrical resistivity of a metal as an example of the interaction between electrons and lattice.

The core ions also contain electrons, but we are able to separate these from the valence electrons in much the same way as it is done in the many electron atom. We *define* a core electron as one which does not respond to the specifically crystalline field. This is simply a matter of definition for any practical case; if an electron has an orbit which is large enough to overlap the neighboring atoms, then we call it a valence electron, otherwise, it is a core electron.

### 1. Free Electrons in a Box

Before starting the main body of our discussion, we shall make a few remarks about a very simple model of a solid. This is the model of the free electrons in a box. Many times in our later work, we shall find a correspondence to the results of this model, and it will be important to have it well in mind. Indeed, some of the simplest metals are reasonably well represented on the model.

Let us take a cube with side  $L$ , assume that at the edge of the cube the potential makes an infinite jump, and that inside the cube the potential is zero everywhere. Let us assume there are  $N$  electrons in the box. The Schrödinger equation for a single electron inside such a cube was solved in Vol. I, Chapter 3, § 1.2: the wave function  $\psi$  and energy  $E$  are given by

$$\psi = A \sin(k_x x) \sin(k_y y) \sin(k_z z), \quad E = \hbar^2 k^2 / 2m \quad (1)$$

with

$$k_x = \frac{n\pi}{L}, \quad n = 1, 2, \dots$$

etc.,

$$k_x^2 + k_y^2 + k_z^2 = k^2.$$

It will be convenient to use exponential wave functions rather than the sinusoidal functions of (1). In order to do this, we make a slight change in the boundary conditions for the problem. Instead of requiring that the wave function becomes exactly zero at the boundary of the box, let us instead think of the box as a three-dimensional periodic box, with periodicity  $L$  in each of the coordinate directions (Vol. I, Chapter 4, § 1). In this case

$$\psi = A \exp(i\mathbf{k} \cdot \mathbf{r}), \quad E = \hbar^2 k^2 / 2m \quad (2)$$

with

$$k_x = \frac{2\pi n}{L}, \text{ etc.}, \quad k_x^2 + k_y^2 + k_z^2 = k^2, \quad n = \dots -2, -1, 0, 1, 2, \dots \text{ etc}$$

In the solutions, (2), the addition of the length  $L$  to any coordinate direction leaves the wave function unchanged.

There is a very good reason for using the periodic or Born-von Kármán boundary conditions. They dispense with surface problems. With the periodic boundary conditions, there is no place where the wave functions go to zero, and they are everywhere homogeneous. On the other hand, in (1), the surface planes through the origin and at  $x, y, z = L$  introduce purely surface effects in the electron density function, etc., which we would like to eliminate in a discussion of bulk properties.

The energy of an electron with wave vector  $\mathbf{k}$  is simply  $E = \hbar^2 k^2/2m$ , where  $m$  is the mass of the electron. If the temperature  $T$  is zero the system of  $N$  electrons is in its lowest state, which means that the lowest  $N$  states of the single electron wave functions (2) are filled. Each allowed point in  $\mathbf{k}$ -space represents two states (counting spin), and the number of states in a spherical shell of thickness  $dk$  is

$$n(k) dk = 8\pi k^2 \left( \frac{L}{2\pi} \right)^3 dk. \quad (3)$$

The integral of (3) yields the maximum value of  $k$  when  $N$  states are filled, and finally, we have the maximum energy is

$$E_f = \frac{\hbar^2}{8mL^2} \left( \frac{3N}{\pi} \right)^{2/3} = \frac{\hbar^2}{2m} k_{\max}^2. \quad (4)$$

This energy is called the Fermi energy of the system.

When  $T$  is not zero as we have assumed above, Fermi-Dirac statistics must be employed. In all cases of interest to us, the temperature will be low enough that the Fermi gas is in a state of extreme degeneration. The fraction of the total number of electrons which are excited is very small. This fact is easily seen when the temperature corresponding to the Fermi energy is computed.  $T_f \approx 10^4$  °K for a typical metal.

With the help of the formulas of the last chapter and the ones of this section, one could proceed to calculate the average energy as a function of temperature, the specific heat, the susceptibility, and so forth for the free electron gas.

A more accurate theory with better wave functions shows that the *form* of these formulas is in many cases correct even for cases where the free electron model is not applicable. However, some of the physical constants which appear must be considered as *parameters* which are to be calculated on the basis of another theory. For instance, the charge on the electron for bands that are nearly full must be taken as positive, and the mass of the electron must be looked on as a parameter which may differ from the mass of the free electron. This picture of the electrons in a solid is called the effective mass approximation.

## 2. The One-Electron Approximation

If we write down the Schrödinger equation for the entire solid, we have something like the following.

$$H(\mathbf{X}_1, \mathbf{X}_2, \dots; \mathbf{x}_1, \mathbf{x}_2, \dots) \Psi(\mathbf{X}_1, \mathbf{X}_2, \dots; \mathbf{x}_1, \mathbf{x}_2, \dots) = E_i \Psi(\mathbf{X}_1, \mathbf{X}_2, \dots; \mathbf{x}_1, \mathbf{x}_2, \dots). \quad (5)$$

Here the wave function,  $\Psi$ , is a function of both the electronic coordinates  $\mathbf{x}$ , and the atom core coordinates  $\mathbf{X}$ . The Hamiltonian contains all the interactions between the electrons as well as the interactions of the valence electrons with the atomic cores, or lattice.

The first reduction of (5) which we shall consider is to tie the core electrons to the nuclear or lattice coordinates. In practice, we treat the core electrons as if they are on free atoms or ions of the proper sort, and take the results of the Hartree calculations for their wave functions. This procedure cannot be far wrong for electrons whose wave functions do not overlap the neighbouring atoms in the resultant solid. As we have said, it is a matter of judgment when to call an electron a valence electron and when to call it a core electron, and any particular assignment will depend on the kind of calculation under way. The category in which an electron belongs depends on the lattice spacing which is the final solution of the problem, so we need to know the answer before we start, so to speak. In (5), we have allowed the internuclear distance to take any values, but in practice we know that a given solid has a crystalline structure, and the nuclear motion is only a very small motion about the equilibrium positions of the lattice. Thus, it will depend on the accuracy desired and the amount of work one is willing to do, whether one takes the free atom Hartree wave functions for an electron, or includes it in a larger band calculation. An example of a case where it is difficult to make the proper choice is the  $d$  shell electrons of the transition elements. The results of the experiments and theory of ferro- and antiferromagnetism suggest that one must use the band theory for these electrons, even though the resultant band is quite narrow compared with the usual valence band.

When the decision is finally made about the core-band category, then one can, from the Hartree functions, work out potential functions between the ion cores amongst themselves, and the potential between the electrons and the cores. Let us call  $V_i(\mathbf{X}_1, \mathbf{X}_2, \dots)$  the potential function amongst all the ion cores, and  $V(\mathbf{X}_1, \mathbf{X}_2, \dots; \mathbf{x}_1, \mathbf{x}_2, \dots)$  the potential function of all the electrons with the ion cores.

If we invoke the Born-Oppenheimer theorem, the Schrödinger problem (5) breaks into two parts. The total wave function becomes a product function  $\Psi = \phi(\mathbf{X}_1, \mathbf{X}_2, \dots)\psi(\mathbf{X}_1, \mathbf{X}_2, \dots; \mathbf{x}_1, \mathbf{x}_2, \dots)$ . Here  $\phi$  is the wave function describing the motion of the ion cores, or "lattice motion," and satisfies a Schrödinger equation of the form

$$\left\{ \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + [V_L(\mathbf{X}_1, \mathbf{X}_2, \dots) + E(\mathbf{X}_1, \mathbf{X}_2, \dots)] \right\} \phi = E_L \phi. \quad (6)$$



$\nabla_i^2$  operates on the lattice coordinates  $\mathbf{X}_i$ , and  $V_L(\mathbf{X}_1, \dots)$  is the potential of the lattice defined above. The function  $\psi$  is the electronic wave function, but is a function of both the lattice coordinates as well as the electron coordinates. The equation it satisfies is

$$\left[ \sum \frac{\hbar^2}{2m_i} \nabla_i^2 + V(\mathbf{X}_1, \mathbf{X}_2, \dots; \mathbf{x}_1, \mathbf{x}_2, \dots) \right] \psi = E(\mathbf{X}_1, \mathbf{X}_2, \dots) \psi. \quad (7)$$

Here, the lattice coordinates are taken as parameters to be varied in an adiabatic way. The electronic energy eigenvalue  $E(\mathbf{X}_1, \mathbf{X}_2, \dots)$  is then

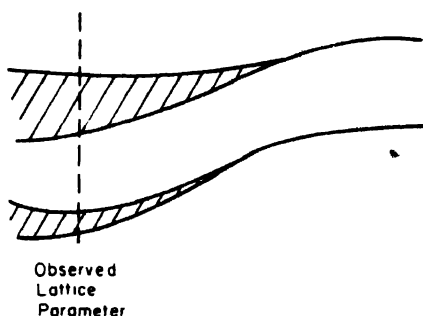


FIG 1 A schematic diagram of how the atomic levels of the atoms change and split into bands as the atoms of the crystal are brought closer together. Deeper levels, corresponding to little overlap, do not split as much as the higher valence levels.

plotted as a function of the normal coordinates of the lattice, and is used in (6) as a part of the potential function. It is the solids counterpart of the Morse function in the theory of molecules

The lattice-valence electron breakdown which we have described is not entirely rigorous because of the electron-lattice interaction, and is only true in first order. In fact, when the interaction is large, as in the case of the ionic crystals, we are not allowed to make the breakdown at all, but must include electron coordinates in the lattice functions.

The problem we have set up in the previous paragraph is indeed formidable, and if it could be solved, we could presumably predict the crystal structure of any solid. A prediction of this kind cannot be made at present from first principles. Hence, ordinarily, we assume that we know the crystal type from experiment, and usually it is also necessary to take the lattice parameter itself as known. Then (7) is an ordinary Schrödinger equation for all the electrons of the solid in a static lattice. (The problem of small nuclear motions will be a later topic.)

Thus our problem is simplified to the classical problem of solids theory: the solution of the Schrödinger equation for the valence electrons, given the potential of a perfectly periodic crystal structure. Equation (7) can now be written as

$$\sum \frac{\hbar^2}{2m_i} \nabla_i^2 + V(\mathbf{x}_1, \mathbf{x}_2, \dots) \big| \psi = E\psi. \quad (8)$$

The potential  $V(\mathbf{x}_1, \mathbf{x}_2, \dots)$  is the potential of the electronic system in a static lattice of ion cores. It contains both the potential of the electrons with the ion cores, which is simply a sum of terms for each electron, as well as the interaction of the electrons with each other. The interaction of the electrons with the cores is the simplest part of the problem because presumably the potential may be computed on the basis of the numerical results for the atomic Hartree functions, as we have mentioned before. If the electron-core interaction were the only term in the potential, the Schrödinger equation would be separable, because this part of the potential is a simple sum over each electron. However, the interaction of the electrons with themselves in the case of a metal is not so simple, because it contains as its most important term a sum over the Coulomb interactions between the individual electrons,  $e^2/r_{ij}$ . This part of the potential makes the Eq. (8) nonseparable, and represents the essential difficulty of the classical problem of the theory of solids. There are other potential terms in the electron interaction besides the coulomb term, namely the spin interactions, but these terms are ordinarily much less important than the ones we have mentioned, except for interactions in which the spin interactions are specifically studied. The electron correlation terms are not important, of course, when the number of electrons in the band under consideration is negligible, as for instance in the excited bands of insulators or semiconductors.

There are two ways we might try to proceed. We might try to keep the *troublesome terms*, and attempt a transformation of the problem as it stands into something more tractable. A simpler method would be to hope, and it is at this stage not more than a hope, that the electron correlation effects due to the coulomb repulsion terms are not important, and that reasonable answers may be obtained by working with only the simpler interaction of the electrons with the ion cores. This second method is the one which has been used in by far the largest part of the theoretical work on solids to date. We shall now discuss some of the reasons why it is as successful as it has been.

part of the reason why other methods are not used is that theories of the correlation terms are only recently being

discovered. Wigner<sup>1</sup> did the pioneer work in an attempt to include the correlation terms, but it has not been till recent years that fundamental progress has begun on the problem. Bohm and Pines<sup>2</sup> and others have developed a method of treating the problem which focuses attention on the correlation forces themselves, and provides a good deal of insight into the way they behave and the effects to be expected. We shall return in § 4 to a short discussion of some of the simpler features of these attempts to treat the many-body problem, but for the time being, we shall concentrate on the successes of the traditional one-electron treatment.

Off hand, one would not expect this mode of treatment to show much correspondence to the physical results, because the coulomb forces between the electrons would be expected to be as large as the forces between the ion cores and the electrons. What happens is that a kind of screening occurs which we shall discuss more at length in § 4, with the result that the one-electron approach has a wide applicability.

## 2.1 Hartree and Fock Methods in Solids

In the one-electron approximation, one attempts to solve Eq. (8) in the way suggested by either Hartree or the later modification of Fock. According to Hartree, we try a solution of the type

$$\psi(\mathbf{x}_1, \mathbf{x}_2 \dots) = \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2) \dots, \quad (9)$$

and by a variational procedure, find the proper equation to solve for the one-electron wave function,  $\psi_i(\mathbf{x}_i)$ . The derivation of the one-electron equation is precisely the same as has already been given for the atomic case (Chapter 1, § 13, in this volume), and the result is

$$H\psi_i(\mathbf{x}_i) = E\psi_i(\mathbf{x}_i) \quad (10)$$

The effective one-electron Hamiltonian is

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V_i(\mathbf{x}_i) + e^2 \sum_j' \int \frac{\psi_j^*(\mathbf{x}_2)\psi_j(\mathbf{x}_2)}{r_{12}} d(\mathbf{x}_2). \quad (11)$$

In (11), we do not sum over the wave function,  $\psi_i(\mathbf{x}_i)$ , which is the solution of (10). The potential  $V_i(\mathbf{x}_i)$  (where we shall sometimes drop the subscript  $i$  when the meaning is clear) is the potential of a single electron in the field of all the ion cores, and the last term is simply the average coulomb energy of electron 1 in the field of all the other electrons.  $r_{12}$  is the distance  $|\mathbf{x}_1 - \mathbf{x}_2|$ .

The method of Fock takes into account that the Pauli exclusion principle must be satisfied, and attempts to solve (8) with a better starting solution, namely the determinant solution,

$$\psi(\mathbf{x}_1; \mathbf{x}_2 \dots) = \frac{1}{\sqrt{N!}} \begin{bmatrix} \psi_1(1) & \psi_1(2) & \psi_1(3) & \dots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & \dots & & \\ \vdots & & & & \\ \psi_N(1) & \dots & & & \psi_N(N) \end{bmatrix} \quad (12)$$

Again, with the use of the variation theorem, one can show that the one electron function,  $\psi_i(\mathbf{x}_1)$ , must satisfy the equation,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_i(\mathbf{x}_1) + V_i \psi_i(\mathbf{x}_1) + e^2 \left[ \sum_j \int \frac{\psi_j^*(\mathbf{x}_2) \psi_j(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2 \right] \psi_i(\mathbf{x}_1) - \quad (13)$$

$$e^2 \left[ \sum_j^{||\text{spin}} \int \frac{\psi_j^*(\mathbf{x}_2) \psi_i(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2 \right] \psi_i(\mathbf{x}_1) = E \psi_i(\mathbf{x}_1).$$

This equation does not even have the form of a Schrödinger equation, because of the last term on the left-hand side. The summation is over all the  $\psi_j$  functions, and the wave functions have been thoroughly mixed up by the operation of a permutation operator. One can, however, interpret the difficult term as due to the exchange charge density,  $\psi_j^*(\mathbf{x}_2) \psi_i(\mathbf{x}_2)$ . We refer the reader to an excellent discussion by Slater<sup>3</sup> on the physical meaning of these terms in the Fock equation. The equation can be forced to have the conventional Schrödinger form,  $H\psi_i(\mathbf{x}_1) = E\psi_i(\mathbf{x}_1)$ , by writing the Hamiltonian as

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V_i + e^2 \left[ \sum_j \int \frac{\psi_j^*(2) \psi_j(2)}{r_{12}} d\mathbf{x}_2 \right] - \quad (14)$$

$$e^2 \sum_j^{||\text{spin}} \int \frac{\psi_j^*(2) \psi_i^*(1) \psi_i(2) \psi_j(1)}{r_{12} \psi_i^*(1) \psi_i(1)} d\mathbf{x}_2.$$

In this equation, we have multiplied and divided the exchange term by the quantity  $\psi_i^*(1) \psi_i(1)$ . Lastly, we note that the exchange term is only summed over those states in which the spins are the same.

The one-electron problem is now well defined. If the correlation due to the coulomb forces between the electrons is neglected, the electrons of the solid satisfy either the Hartree or Fock equations, depending on whether the spin correlations are included. At this stage, there are two fundamentally different paths to take in the solution of the equations. One corresponds

## 6. THEORY OF SOLIDS

to the treatment given by Heitler and London in the theory of molecules, and the other to the Hund and Mulliken approach. One can, in short, either localize a given electron wave function about a particular site of the crystal, or one can make the wave function spread out over the entire crystal. We note one possible error in thinking at this point. When we "localize" the electron in the Heitler-London treatment of the Fock equation, we do not mean that the electrons are distinguishable and actually localized on particular atom sites. But the *one-electron wave function* from which we build up the determinantal solution of the Fock equation is localized in space. In the alternative Hund-Mulliken or Bloch procedure, the one-electron functions themselves are spread throughout the crystal.

Suppose that we wished to solve the Fock equation with the Heitler-London technique. Then the wave function is the determinant (12) and we seek a solution of the Hamiltonian (13) which is localized about a particular atomic site. That a solution of this type probably exists is shown by the fact that if the other atoms of the lattice are sufficiently far away, the problem is simply that of a single isolated atom or ion. Indeed, we can use the solution of the isolated ion or atom in what would seem to be rather crude approximation of the correct result. However, the principal error in a straightforward substitution of the atomic orbitals into the final determinantal solution is the fact that some overlap occurs between neighbours, and the one-electron functions,  $\psi_i(\mathbf{x})$ , are not orthogonal. One of the specific assumptions of the derivation of the Fock equation is that the one-electron function,  $\psi_i(\mathbf{x})$ , which is isolated at the atomic site  $\mathbf{R}_i$ , is orthogonal to any other function  $\psi_j(\mathbf{x})$  localized at any other point  $\mathbf{R}_j$ . There are various tricks for orthogonalizing a set of one-electron functions by taking linear combinations of the set. However, we refer the reader to the literature for these special procedures.<sup>4</sup>

### 2.2 The Bloch Theorem

The alternative to the Heitler-London method is the one that is analogous to the Hund-Mulliken method in the theory of molecules, where the one-electron function is spread out over the entire crystal. Bloch is the originator of the method when applied to solids, and proved the basic theorem which is that one of the solutions of the Fock equation (13) is

$$\psi_{\mathbf{k}}(\mathbf{x}) = e^{i\mathbf{k} \cdot \mathbf{x}} u_{\mathbf{k}}(\mathbf{x}). \quad (15)$$

The solution (15) is called a Bloch wave, and the function  $u_{\mathbf{k}}(\mathbf{x})$  is periodic in the lattice. That is,

$$u_{\mathbf{k}}(\mathbf{x} + \mathbf{R}_j) = u_{\mathbf{k}}(\mathbf{x}). \quad (16)$$

$\mathbf{R}_j$  is the vector between the origin (assumed to be at a lattice point) and any other lattice point of the crystal.  $\mathbf{R}_j$  is called a lattice vector.

Bloch's theorem is in its essence a result of the translational symmetry of the crystal. Thus the Hamiltonian for the crystal commutes with all the elements  $T_i$  of the basic translation group of the crystal. The elements of the translation group also commute with each other. The translation operators are just those which satisfy the equation

$$T_i \mathbf{x} = \mathbf{x} + \mathbf{R}_i. \quad (17)$$

Hence, it is possible to choose solutions of the Fock equation which diagonalize simultaneously the Hamiltonian and all the translation operators. The result of operation on one of these wave functions with any of the translation operators must be to multiply the wave function by a constant of absolute value 1. We choose to write this constant in a particular way:

$$\psi_{\mathbf{k}}(\mathbf{x}) = e^{-i\mathbf{k} \cdot \mathbf{R}_j} \psi_{\mathbf{k}}(\mathbf{x} + \mathbf{R}_j). \quad (18)$$

This way of writing the constant points to the fact that when we operate twice with two displacement operators, the result on the wave function is a translation by the sum of the two individual translations. The exponential form of the constant automatically gives us this result. Equation (18) is essentially a definition of  $\mathbf{k}$ .

If we multiply Eq. (18) by  $e^{-i\mathbf{k} \cdot \mathbf{x}}$ , then

$$e^{-i\mathbf{k} \cdot \mathbf{x}} \psi_{\mathbf{k}}(\mathbf{x}) = e^{-i\mathbf{k} \cdot (\mathbf{x} + \mathbf{R}_j)} \psi_{\mathbf{k}}(\mathbf{x} + \mathbf{R}_j), \quad (19)$$

which shows that  $e^{-i\mathbf{k} \cdot \mathbf{x}} \psi_{\mathbf{k}}(\mathbf{x}) = u_{\mathbf{k}}(\mathbf{x})$  is periodic in the crystal. Hence, we can write  $\psi_{\mathbf{k}}(\mathbf{x})$  in the form of Bloch

$$\begin{aligned} \psi_{\mathbf{k}}(\mathbf{x}) &= e^{i\mathbf{k} \cdot \mathbf{x}} u_{\mathbf{k}}(\mathbf{x}), \\ u_{\mathbf{k}}(\mathbf{x}) &= u_{\mathbf{k}}(\mathbf{x} + \mathbf{R}_j). \end{aligned} \quad (20)$$

We have introduced in Bloch's theorem a general solution to the one-electron equation which has the form of a modulated plane wave. It is a kind of marriage of the solutions of the particles in a box problem with the more atomic like functions,  $u_{\mathbf{k}}(\mathbf{x})$ , which are centred about the lattice sites,  $\mathbf{R}_j$ . In the tight binding approximation of the next section, we shall take precisely this point of view.

With the introduction of plane waves into the solution, we have also introduced the propagation vector  $\mathbf{k}$ , and there are some important relations involving vectors in  $\mathbf{k}$ -space which are related to the symmetry of the crystal that we shall now demonstrate. First of all, we still assume that the crystal satisfies the periodic boundary conditions which we explained in connection

with the box problem. The wave function  $\psi_{\mathbf{k}}(\mathbf{x})$  must be periodic with periodicity  $L$  in each of the coordinate directions. Since  $u_{\mathbf{k}}(\mathbf{x})$  is already periodic in the lattice, the plane wave  $e^{i\mathbf{k} \cdot \mathbf{x}}$  must then have the periodicity  $L$ , and we have the same conditions on the vector  $\mathbf{k}$  as earlier, namely Eq. (2).

There is a set of  $\mathbf{k}$  vectors which are particularly important, called the reciprocal vectors. They are defined by the relations

$$\mathbf{K}_i \cdot \mathbf{R}_j = n_{ij}, \quad (21)$$

$n_{ij}$  is an integer which depends on  $\mathbf{K}_i$  and  $\mathbf{R}_j$ . The  $\mathbf{K}$  vectors are reciprocal to the lattice vectors,  $\mathbf{R}_j$ , and form in  $\mathbf{k}$ -space a reciprocal lattice to the lattice  $\mathbf{R}_j$ . We shall see the usefulness of the reciprocal vectors in later sections.

The Bloch and Heitler-London methods give rise to two quite different solutions to the problem of electrons in a solid. The question arises, in what cases should the one or the other be used? The most striking difference between the two is that the Bloch method leads to a band of levels (the next section takes up this question in detail), while the Heitler-London method deals primarily with the lowest state of the system. The Bloch solutions are themselves running waves, and thus make a discussion of the conduction properties of metals simpler. With the localized wave functions of the Heitler-London method, running waves have to be constructed by superposing a large number of excited states; while on the other hand, this method is admirably suited to the discussion of an insulator where there is a gap between a full and an unfilled band. One can, in principle, construct a band of levels by superposing excited states, but the procedure becomes very cumbersome, and the results would be equivalent to the Bloch approach if enough excited states are introduced. We gain further insight into the difference between the two methods when we note that when the atoms of the solid are far removed from each other, the solution of the problem must resemble the solution of free atoms, and hence the Heitler-London solution is most appropriate. However, for very small lattice spacings, the Bloch solution is most appropriate because of the large amount of overlap between the wave functions. Hence, summing up, Heitler-London solutions are used for insulating solids like the ionic crystals, diamond, and the lowest level of semiconductors. The Bloch method is used for metals and to discuss the empty bands in semiconductors.

We do not mean to imply that the Heitler-London and Bloch solutions are intrinsically different from one another, and indeed it has been shown that they are equivalent for closed shells or filled bands. But they each lead to somewhat different physical pictures of the solid and suggest different

ways of making further approximations. For example, we may calculate the cohesive energy of the NaCl crystal either from the point of view of the band theory or the Heitler-London theory. However, the calculations and approximations made in the two methods will be quite different, although the calculated answer should be the same.

### 3. Band Approximation

In this section, we shall turn our attention exclusively to the Bloch treatment of a solid and the connected idea of electron bands. The physical idea of bands has already been given in the introduction to this chapter. There are many different ways of demonstrating their properties analytically. Perhaps the most popular first demonstration is to use perturbation theory on the free electron model. According to this model, one assumes that the atoms contribute a small periodic potential to the free electron "box." However, we prefer to do the problem with a method which has a greater correspondence with reality, and which shows in some detail the correspondence between the atom in its free state and in its condensed crystalline state. We shall, then, illustrate the original tight binding scheme of Bloch<sup>6</sup> and a simplified version of the cellular method of Wigner and Seitz<sup>5</sup> suggested by Bardeen.<sup>7</sup>

#### 3.1 Tight Binding Method

In the tight binding method, we again try to use information about the solution of the atomic problem to solve the solids problem. In particular, let us try to solve the Fock equation (13) using a wave function of the form

$$\psi_{\mathbf{k}}(\mathbf{x}) = \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} \chi(\mathbf{x} - \mathbf{R}_j) \quad (22)$$

The sum is taken over all the lattice sites of the crystal. We rewrite (22) in the form

$$\psi_{\mathbf{k}}(\mathbf{x}) = e^{i\mathbf{k} \cdot \mathbf{x}} \sum_j e^{-i\mathbf{k} \cdot (\mathbf{x} - \mathbf{R}_j)} \chi(\mathbf{x} - \mathbf{R}_j). \quad (23)$$

The summation is now obviously periodic in the crystal, because it is not changed by the substitution  $\mathbf{x} = \mathbf{x}' + \mathbf{R}_l$ , and is thus a Bloch type function. We shall assume that the  $\chi$  functions are solutions of the free atom wave equation. We write the Fock or Hartree equation in the one-electron approximation in the form

$$\frac{\hbar^2}{2m} \nabla^2 \psi_{\mathbf{k}} + V \psi_{\mathbf{k}} = E_{\mathbf{k}} \psi_{\mathbf{k}}. \quad (24)$$



The potential  $V(\mathbf{x})$  is the "crystal potential," which we compute either according to the Fock or Hartree prescriptions. With the substitution of (22), it becomes

$$\sum_{\mathbf{R}_j} e^{i\mathbf{k} \cdot \mathbf{R}_j} \left\{ -\frac{\hbar^2}{2m} \nabla^2 \chi(\mathbf{x} - \mathbf{R}_j) + V \chi(\mathbf{x} - \mathbf{R}_j) = E_{\mathbf{k}} \chi(\mathbf{x} - \mathbf{R}_j) \right\} \quad (25)$$

We write the Schrödinger equation for the free atom as

$$\frac{\hbar^2}{2m} \nabla^2 \chi(\mathbf{x} - \mathbf{R}_j) + V_a \chi(\mathbf{x} - \mathbf{R}_j) = E_a \chi(\mathbf{x} - \mathbf{R}_j).$$

$E_a$  is in effect the ionization energy of the atom. We should have written a subscript on  $\chi$  to show which atomic orbital is being used, but we have suppressed it for clarity since at any stage, we shall always be concerned with only one type of atomic orbital. Finally, Eq. (25) becomes

$$(E_{\mathbf{k}} - E_a) \sum_{\mathbf{R}_j} e^{i\mathbf{k} \cdot \mathbf{R}_j} \chi_j = (V - V_a) \sum_{\mathbf{R}_j} e^{i\mathbf{k} \cdot \mathbf{R}_j} \chi_j. \quad (26)$$

We have used  $\chi_j$  as short for  $\chi(\mathbf{x} - \mathbf{R}_j)$ . We now use one of the standard tricks of quantum mechanics, and multiply Eq. (26) by  $\chi_m^*$ , then integrate over the variable  $\mathbf{x}$ . There will be some terms like

$$\int \chi_m^* \chi_j d\mathbf{x}, \quad m \neq j$$

in the result. The essential approximation of the original Bloch tight binding method is to neglect these, because if an electron is "tightly bound" to an atom it will not overlap appreciably in the solid. However, if we are able to construct functions which are linear combinations of the atomic functions, and are really orthogonal to one another in the above sense, then the integrals will be rigorously zero, while the functions themselves still satisfy the free atom Schrödinger equation. This is one of the possible modifications of the Bloch tight binding procedure. The other is to retain the overlap terms throughout the discussion. For the moment, we simply assume that the functions on different lattice sites are orthogonal, either because they belong to tightly bound electrons, or are artificially constructed orthogonal by some independent method. With these assumptions, the equation can ultimately be written

$$E_{\mathbf{k}} = E_a + \sum_{\mathbf{R}_j} e^{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_m)} \int \chi_m^* (V - V_a) \chi_j d\mathbf{x} \\ = E_0 + \sum_{\mathbf{R}_j} e^{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_m)} V'_{mj}. \quad (27)$$

Equation (27) gives the electronic energy of the lattice as the atomic binding energy plus a correction term which is essentially the matrix element of the difference between the crystalline and free atom potentials, summed over all the lattice sites of the crystal.

If the electron is tightly or nearly tightly bound, then the term for the reference site and those for the nearest neighbors are the most important terms of the crystal summation. This approximation gives us the band splitting results we seek, and we shall now restrict ourselves to this case. Suppose we have a set of atoms all of the same type distributed on a simple cubic lattice with lattice constant  $a$ . The sum (27) performed over the atom at the origin and the nearest shell of atoms about the atom at the origin becomes

$$E_{\mathbf{k}} = E_a + V'_0 + 2V'_1 (\cos k_x a + \cos k_y a + \cos k_z a),$$

$$V'_0 = \int \chi_i^* (V - V_a) \chi_i d\mathbf{x}, \quad (28)$$

$$V'_1 = \int \chi_i^* (V - V_a) \chi_j d\mathbf{x}.$$

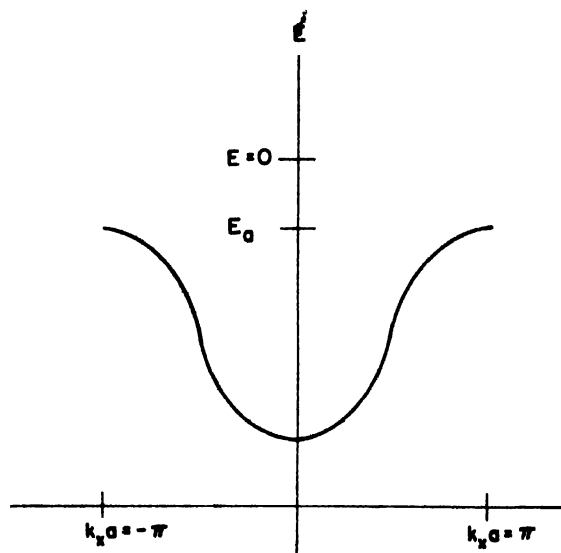


FIG. 2. A plot of Eq (28) along the  $k_x$  direction. We have chosen the basic periodicity region to extend from  $k_x = -a$  to  $k_x = a$ . Note that the band we have drawn has a minimum at  $k = 0$ , which would be true for  $s$  functions. The band also corresponds to a case of positive binding because the average energy of the band lies below the free atom energy,  $E_a$ .

$V'_0$  is the matrix element of  $V'$  for the atom at the origin,  $V'_1$  is the same quantity for the nearest shell. Equation (28) shows that for each atomic energy level, we can expect a spreading out of the energy eigenvalues of the crystal. We have sketched the  $E(k)$  in the  $k_x$  direction in Fig. 2, where the energy has a minimum at  $k_x = 0$ . This is the situation one would expect for  $s$  type  $\chi$  functions, and corresponds to the potential difference term,  $V'$  being negative (Binding will occur only if  $V'$  is negative!)

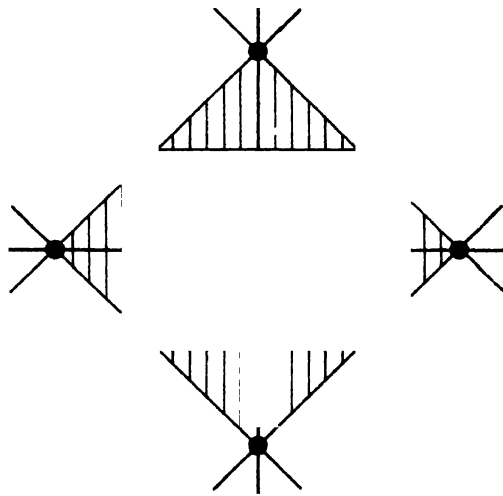


FIG 3 Brillouin's construction in two dimensions for a cubic lattice. The zone boundaries are made up of the planes which are the perpendicular bisectors of the  $\mathbf{K}$  vectors. The perpendicular bisectors for the first four  $\mathbf{K}$  vectors around the origin in  $\mathbf{k}$ -space form a square, which we have cross-hatched horizontally. This first zone is the only one we have discussed, and it is sufficient to limit one's discussion to it; however, for some purposes, it is convenient to include higher zones. The construction for the second zone proceeds as before, and is made up of the next region formed by the bisecting planes to more distant  $\mathbf{K}$  vectors. We note that the total area of the sectors which make up the second zone is just equal to the area of the first zone.

Equation (28) is periodic in  $\mathbf{k}$ -space, and repeats itself in each of the cells defined by the reciprocal vectors of (21). That is, if we add any of the reciprocal vectors to a given  $\mathbf{k}$ , then the energy is unchanged. For this reason, one usually only plots the energy in one cell, remembering that it is repeated in all others. Hence in our Fig. 2, we have only drawn the energy in the  $\mathbf{k}$ -space cell enclosing the origin. Obviously, the way in which one

chooses the shape of the boundary of the basic cell is quite arbitrary, and will be chosen in one type of problem in a slightly different way than in another. It is only important to choose a cell which contains a complete region of periodicity.

The construction of Brillouin for a two-dimensional crystal is shown in Fig. 3. A complete zone of periodicity is usually called a Brillouin zone. We have shown in Fig. 4 two of the more common three-dimensional first

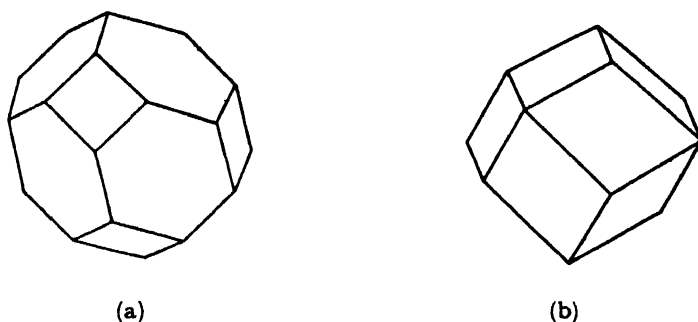


FIG. 4. (a) The Brillouin zone of the face centered cubic crystal. The lattice of the reciprocal vectors is a body centered cubic lattice. (b) The Brillouin zone of the body centered cubic lattice. The  $\mathbf{K}$  vectors form a face centered cubic lattice (J. Reitz).

Brillouin zones. We note that the cubic lattice has a cubic zone, while the zones for the body centered and face centered lattices are more complicated.

There is a further sense in which the division of  $\mathbf{k}$ -space into zones is "complete." It can be shown, and we leave it as an exercise to the reader to demonstrate it in the case of the cubic crystal, that the number of allowed  $k$ -values in the lowest zone is just equal to the number of atoms in the crystal. Since each of the periodicity zones in  $\mathbf{k}$ -space has the same volume, the statement also holds true for all the zones. Thus if we start in each of  $N$  atoms with a single nondegenerate atomic orbital, then there will be  $N$  states in each Brillouin zone. Usually, the atomic orbital has spin degeneracy, and, for example, the  $^2S_{1/2}$  orbital will lead to  $2N$  levels.

It is very instructive to compare the energy as a function of  $k$  which we have just calculated with the energy of  $N$  free electrons in a box the size of the crystal. The energy of the free electrons is simply  $E = (\hbar^2/2m)k^2$ . For small values of  $k$ , we can expand (28) to obtain a similar expression quadratic in  $k$ :

$$E_{\mathbf{k}} = E_s + V'_0 + 6V'_1 - V'_1 a^2 k^2. \quad (29)$$

## 6. THEORY OF SOLIDS

In order to force the form of (29) to be the same as the expression for free electrons, we can define an effective mass  $m^*$  to be

$$m^* = \frac{1}{2a^2 V_1'} \quad (30)$$

One can show that under the action of electric field in the crystal, the electrons will actually accelerate as if they possessed the mass  $m^*$  (see Eq. 97).

We note one other characteristic feature. If the energy is expanded about one of the cube corners of the Brillouin zone, one also obtains a quadratic function in  $k$ , but since the curvature of the  $E(k)$  function is negative there, the effective mass is negative. The "particles" accelerate in the opposite direction to which they should in a field. This phenomenon is called hole conduction. Instead of looking at the electron behavior, if we had noticed that the Brillouin zone is nearly full except for some "holes" in the distribution near the top, we could say that these holes appear as positive charges in the full band. So instead of saying that the mass is negative, it is usual to say that the mobile entities at the top of the band are actually the holes in the otherwise full Fermi sea. They behave as if they have a positive mass  $m^*$  and a positive electronic charge.

At all other points in the Brillouin zone, the curvature of the  $E(k)$  function is complicated, and a single effective mass is not defined, but will depend on the direction of the field.

The periodicity of the energy function in  $k$ -space is not a property which is restricted to the present model. We can show quite easily that the periodicity and the resultant concept of energy levels interspersed between other bands of forbidden regions is due simply to the Bloch form of the solutions, (15). The energy periodicity theorem rests upon the fact that two wave functions which differ from each other in their values of  $k$  by a reciprocal vector, that is,  $k - k' = K$ , are essentially equivalent to each other. Hence the energy calculated from the one is equal to the energy calculated from the other.

It will be convenient in the demonstration of this theorem and for some of our later work as well to write out the equation satisfied by the  $u_k(\mathbf{x})$  functions. If we substitute the Bloch form of the solution into the Fock equation, a simple series of steps leads to the equation we seek,

$$-\frac{\hbar^2}{2m} (\nabla^2 u_k - 2i\mathbf{k} \cdot \nabla u_k) + V u_k = (E_k - \frac{\hbar^2 k^2}{2m}) u_k. \quad (31)$$

$V(\mathbf{x})$  is the crystalline potential of the one-electron problem, discussed earlier.

Assume that we have two wave functions,  $\psi_{\mathbf{k}}(\mathbf{x})$  and  $\psi_{\mathbf{k}'}(\mathbf{x})$ , such that

$$\begin{aligned}\psi_{\mathbf{k}} &= e^{i\mathbf{k} \cdot \mathbf{x}} u_{\mathbf{k}}, \\ \psi_{\mathbf{k}'} &= e^{i\mathbf{k}' \cdot \mathbf{x}} u_{\mathbf{k}'}\end{aligned}\tag{32}$$

The vectors  $\mathbf{k}$  and  $\mathbf{k}'$  are related by

$$\mathbf{k}' - \mathbf{k} = \mathbf{K}.$$

With this substitution, the second Eq. (32) becomes

$$\psi_{\mathbf{k}'} = e^{i\mathbf{k} \cdot \mathbf{x}} [e^{i\mathbf{K} \cdot \mathbf{x}} u_{\mathbf{k}'}],$$

where the quantity in brackets has the form of another  $u_{\mathbf{k}}$  function; that is, it is periodic in the crystal. The new function,  $u_{\mathbf{k}'}$ , must hence satisfy the same Eq. (31) as the first function (31) does, since it goes with the same exponential  $e^{i\mathbf{k} \cdot \mathbf{x}}$ , and is likewise periodic. It must therefore have the same value of the energy  $E(k)$ , which proves the theorem.

We have already mentioned that the approximation which makes the present form of the tight binding method inapplicable to the usual crystal problem is the neglect of the overlap integrals due to the fact that the atomic orbitals in actuality extend considerably further than the interatomic distance in the solid. There are two ways to remedy the situation: the present method could be used, except that terms greater than nearest neighbor interactions must be taken into account in Eq. (37), and the overlap terms must be kept and treated explicitly. The second method, which is just equivalent to the first, is to develop a set of functions like the atomic orbitals which are centered about specific lattice sites, but constructed in such a way that the function centered about one lattice site is rigorously orthogonal to those centered about all other sites. (See § 7.1) This extended *tight binding* type of calculation has been applied in an important way to the valence electrons of a solid by Slater and Koster.<sup>8</sup> The method is exceedingly tedious to use because the overlap terms add greatly to the complication of the numerical work, but with the use of computer machines, the method seems to have a future.<sup>10</sup>

### 3.2 Cellular Method

We shall now continue our discussion of band structure by developing a slightly different point of view of the problem, which was first suggested by Wigner and Seitz<sup>5</sup> in their paper on the cohesion of metals. The so-called *cellular method* proposed by these authors affords a particularly useful picture of what happens to the wave functions of the electrons when the atoms are brought together in the solid. And from this picture, it is easy to see what the basic mechanism of metallic cohesion is.

The basic idea of the method is to pay particular attention to the way in which the boundary conditions of the Fock equation for the free atom are changed when the atom becomes part of a crystal. Of course, the potential of the Fock equation changes somewhat due to the influence of the other atoms in the vicinity, but in the case of simple metals like Na, this change is not the most important factor. When the atom is placed in the crystal, we can draw a polyhedron around it which is representative of the space of the crystal allotted to the atom. In a perfect cubic crystal, the cell is simply a cube with side equal to the lattice parameter. These cubes with the atoms at their centers fill up the space of the lattice. The space filling cells of the more complicated lattices are obtained in the real lattice space in the same way as the Brillouin zones were constructed in  $\mathbf{k}$ -space. The polyhedron is defined by taking the volume formed by placing perpendicular bisecting planes on the radius vectors between the atom and its various neighbours. The boundary conditions must be specified on the boundaries of the polyhedrons.

We now try to solve the Fock equation in the volume of one of these cells, and choose our boundary conditions on the boundary of the cell so that the wave function of one cell fits smoothly onto the wave function of a neighbouring cell. If we remember that the wave function of the solid has the Bloch form  $e^{i\mathbf{k} \cdot \mathbf{x}} u_{\mathbf{k}}$ , and that the  $u_{\mathbf{k}}(\mathbf{x})$  are periodic between one cell and another, we can focus our attention only on the equation for  $u_{\mathbf{k}}$  in a given cell and its boundary conditions on the boundary of that polyhedron. The function  $u_{\mathbf{k}}(\mathbf{x})$  itself and its first derivatives must be continuous on the boundary between one cell and the next.

Let us consider a specific example for the application of the cellular method. Suppose that the valence electrons are  $s$  electrons, which is the first system to which the method was applied. Then we can replace our polyhedra by spheres around the atoms which have the same volume, and solve the Fock equation in a sphere. If the wave function is to have a continuous first derivative at the boundary, it is then necessary that the first derivative tend to zero there.

The equation for  $u_{\mathbf{k}}$  is given in Eq. (31), and we assume that in the first approximation, the potential function is just the potential of the ion core of the free atom. There is one very simple way of treating this equation, and it is to notice that without the term,  $\mathbf{k} \cdot \nabla u_{\mathbf{k}}$ , the equation has exactly the same form as the Schrödinger equation for the free atom. So it is very tempting to adopt the perturbation procedure for this term. Perturbation theory will, of course, only be applicable for small values of the vector  $\mathbf{k}$ , and for functions  $u_{\mathbf{k}}$  which are reasonably smooth. We note that even

though the Hamiltonian is the same as for the free atom, the boundary conditions are different, and thus the wave functions and eigenvalues will be different.

We shall take up first the change in the wave function. Wigner and Seitz have given the numerical solution of the  $u_k$  equation for  $k = 0$  in the case of the valence electrons of Na for the spherical cell. We have plotted this wave function and the one for the free atom for comparison in Fig. 5.

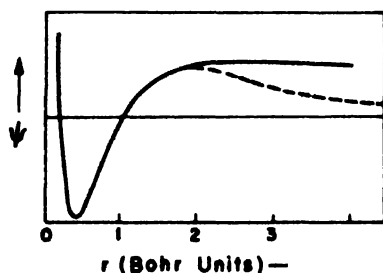


FIG. 5. A comparison of the function  $u_k$  ( $k = 0$ ) for Na with the free atom wave function. The free atom function appears with the dotted tail where it diverges from the  $u$  function.

We note that there are two differences between the two wave functions. First, the  $u_k$  for the crystal is a much smoother function, and thus has a lower kinetic energy than the valence electron of the atom. Also, since the  $u_k$  is normalized to the volume of the sphere instead of throughout all space, the electron density is higher in the region near the atom, and hence the potential energy of the  $u_k$  function is also lower because it is closer to the nucleus and the core. (Of course, there is always

present the compensating effect of the Pauli principle to supply the repulsive force.) Thus the average energy of the  $u_k$  function is lower than that of the free atom valence wave function. This energy is the seat of the binding energy of the metal, and we see that it is due to the change in the boundary conditions of the problem when the atom is put into the crystal.

We have only given a discussion of the  $u_k$  equation for  $k = 0$ , however. When  $k \neq 0$ , the Hamiltonian is not identical to the free atom Hamiltonian, but contains the perturbation term  $i\mathbf{k} \cdot \nabla u_k$ . However, to the extent that perturbation theory is applicable we see from (31) that the zero order energy for  $k \neq 0$  is related to the energy  $E_{k=0}$  by the equation,

$$E^0 = E_{k=0} + \frac{\hbar^2 k^2}{2m}. \quad (33)$$

To the extent that the perturbation can be neglected, Eq. (33) gives us a very suggestive interpretation of the results. The excess energy over the energy at the bottom of the band of an electron when it has a wave vector  $\mathbf{k}$  is  $(\hbar^2/2m)k^2$ . This is just the kinetic energy of a free electron with the same wave vector  $\mathbf{k}$ . Thus we see in an analytic way the manner in which the



electrons of a metal behave approximately as if they were free electrons in a box. Indeed, the condition that (33) really is valid for all  $\mathbf{k}$  is that the  $u_{\mathbf{k}}$  functions are constant. In that case, the perturbation would indeed be zero, the total wave function would be simply the running wave  $e^{i\mathbf{k} \cdot \mathbf{x}}$  and the mass would be the free electron mass. The calculations for the alkali metals show that the wave function  $u_{\mathbf{k}}$  does flatten out to a remarkable degree, as depicted in Fig. 5. Since the wave function oscillates for small  $r$ , and becomes essentially constant for larger  $r$ , *volumewise* the  $u_{\mathbf{k}}$  function is nearly constant over the cell, and the free electron approximation is remarkably good.

We now complete the picture by including the effect of the perturbation term of Eq. (31). We have so far only allowed ourselves to speak of  $s$  type functions. If we still restricted the solutions of (31) to this type, the energy to second order in  $k$  would still be the same as the free electron result. However, the actual solution of (31) should contain functions of higher angular momentum. Indeed, even the solution for  $k = 0$  should contain higher terms, although in the case of the alkali metals, these added terms for  $k = 0$  are small and we will continue to neglect them. We solve (31) with the perturbation expansion

$$u_{\mathbf{k}} = u_0 + u_1 \quad (34)$$

$u_0$  is the unperturbed solution, and we have the equations

$$\begin{aligned} \frac{\hbar^2}{2m} \nabla^2 u_0 + V u_0 &= E_0 u_0, \\ \frac{\hbar^2}{2m} \nabla^2 u_1 + V u_1 &= E_0 u_1 + \frac{i\hbar^2}{m} \mathbf{k} \cdot \nabla u_0. \end{aligned} \quad (35)$$

If we still assume that  $u_0$  is an  $s$  type function, then the second equation (35) shows that  $u_1$  must be an odd function in the origin. Since  $u_1$  must also be periodic from one cell to another, it means that  $u_1$  must change sign from one cell to another. If we replace the polyhedron by the sphere of equal volume our boundary condition can be expressed that  $u_1$  must disappear on the surface of the sphere. The second equation (35) is an inhomogeneous differential equation, and a particular solution to it is the function,

$$i\mathbf{k} \cdot \mathbf{x} u_0(r). \quad (36)$$

In order to satisfy the boundary condition, we have to add to (36) a solution of the homogeneous equation  $v_1(r)$  so that

$$u_1 = i\mathbf{k} \cdot \mathbf{x} [v_1(r) - u_0(r)], \quad v_1(r_s) = u_0(r_s). \quad (37)$$

Our total wave function is now

$$\begin{aligned}\psi_{\mathbf{k}} &= e^{i\mathbf{k} \cdot \mathbf{x}} [u_0(r) + i\mathbf{k} \cdot \mathbf{x}(v_1(r) - u_0(r))] \\ &= e^{i\mathbf{k} \cdot \mathbf{x}} [u_0(r) + u_1(x)].\end{aligned}\quad (38)$$

If we compute the average value of the energy with this wave function, we have, using our previous notation,

$$\begin{aligned}E &= \int (u_0^* + u_1^*)(H_0 + H')(u_0 + u_1) d\mathbf{x} \\ &= \int u_0^* H_0 u_0 d\mathbf{x} \\ &\quad + \int (u_0^* H_0 u_1 + u_1^* H_0 u_0 + u_0^* H_1 u_0) d\mathbf{x} \\ &\quad + \int (u_1^* H_0 u_1 + u_1^* H_1 u_0 + u_0^* H_1 u_1) d\mathbf{x} \\ &\quad + \int (u_1^* H_1 u_1) d\mathbf{x}, \\ H_0 &= -\frac{\hbar^2}{2m^*} \nabla^2 + V, \\ H_1 &= -2i\mathbf{k} \cdot \nabla.\end{aligned}\quad (39)$$

The first term is just the free electron approximation given earlier. The next three first-order terms are zero because the integrands are odd functions. The next three terms are quadratic in  $k$ ; the last is cubic in  $k$ , and we will neglect it because it is of higher order in the perturbation than the other terms. Equation (39) now allows us to write the energy of the electrons in the same form as for free electrons, but with an effective mass. The effective mass is given in terms of the wave functions above by the equation

$$\begin{aligned}E &= E_0 + \frac{\hbar^2}{2m^*} k^2 \\ \frac{m}{m^*} &= 1 + \frac{2m}{\hbar^2} \int (u_1^* H_0 u_1 + u_1^* H_1 u_0 + u_0^* H_1 u_1) d\mathbf{x}.\end{aligned}\quad (40)$$

The procedure we have sketched for the cellular method is that due to Bardeen,<sup>7</sup> and is really only applicable to the alkali metals, where the perturbation theory is valid. An important feature of the theory is the inclusion of the higher angular momentum wave functions.  $u_1$  turns out to be essentially a  $p$  function. The presence of wave functions of the higher

bands is important in other ways. The alkaline earths, in their atomic configuration, have two  $s$  electrons, and if in the solid, there were no mixture with the  $p$  band, we would expect them to be insulators. Such is not the case, and further, we have experimental verification from X-ray evidence that the Ca electrons have a strong intermixture of  $p$  functions.

We shall not trace out in detail any further attempts to extract the wave function of the solid from the theory. Beyond the rather general discussion we have given up till now, most progress has been made by restricting the work to some particular direction in  $\mathbf{k}$ -space. To work out the energy or wave function for any value of the  $\mathbf{k}$  vector is a formidable task, as we have seen. However, if one chooses the value of  $\mathbf{k}$  to lie in a highly symmetric direction of the crystal, then the labour of construction of the wave function is greatly lessened by bringing into play the theorems of group theory, which restrict drastically the family of possible functions which can be used for solutions of the Schrödinger equation. We do not have the space to enter here into a discussion of this subject, but refer the reader to the article by Slater<sup>9</sup> in the *Handbuch der Physik*.

### 3.3 Solid Types on the Basis of Band Theory

In the rest of this section, we shall turn to a short discussion of some of the results of the theoretical work, and make some general comments about the types of band structures found and the consequences of these structures for some of the properties of solids.

One can make an attempt to classify the solids into broad types or categories. Exactly what the categories are, and which solids are included in one and which in another depends on considerable subjective judgment, and the point of view of the general discussion. It perhaps fits best into our discussion to make the classification on the basis of the forces which hold the solid together. There will be many borderline cases where the dividing line is difficult to draw, because in most materials, the total cohesive energy is actually made up of several different contributions. Nevertheless, with this essential ambiguity in mind, we shall list four types: (1) covalent crystals, (2) ionic crystals, (3) metals, and (4) molecular crystals.

#### 3.3.1 Covalent Crystals

The prototype of this class is the diamond crystal. The number of nearest neighbors is usually related to the valence. For example, in diamond, the nearest neighbor shell forms a tetrahedron about the reference atom, while the valence of carbon is four. Qualitatively, the bond in this case

is the same type of bond as is met in molecular binding, and the cohesive energy per atom is of the order of the binding of the carbon atom in saturated molecules. As solids, these cohesive energies are high, compared with the other types. The highest band containing electrons is completely full, with no overlap with other bands. Hence, the crystals are either insulators or

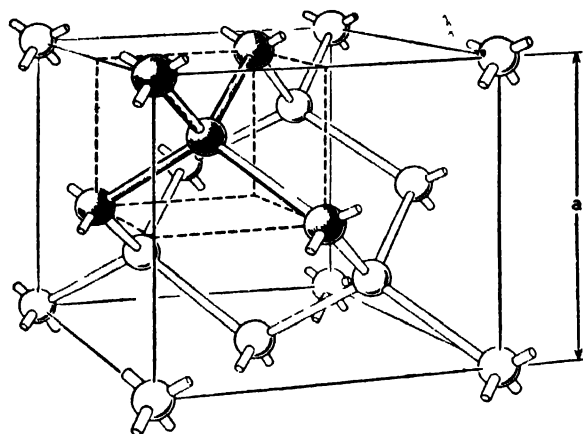


FIG. 6. The diamond lattice. The figure shows the tetrahedral arrangement of nearest neighbors, and also that the lattice is basically two face centred lattices displaced from one another along the body diagonal (W. Shockley)

semiconductors. An intrinsic semiconductor is a covalent crystal in which the separation between the filled band and the next excited band is small enough for thermal fluctuations to throw an appreciable number of electrons into the excited band at ordinary temperatures. Germanium is such a crystal. A very intensive study has recently been made of some of the covalent crystals because of the tremendous practical application of the semiconductors. We shall describe some of the results because they show very beautiful examples of what one can expect from band theory in cases which are somewhat more complicated than the alkali metals.

We have plotted in Fig. 7 the results of two papers on the band structure of diamond. The end points of the curves were calculated by Herman<sup>10</sup> using the orthogonalized plane wave method which is a method of calculating band structure which we have not discussed, but is one of the more powerful modern techniques which have been developed. These points have about as much accuracy as one is able to attain in band calculations. The curves in between them were found by Slater and Koster<sup>8</sup> with the extension of the tight binding method which we have already treated.

We remember that there are four valence electrons in carbon, two  $2s$  electrons and two  $2p$ . At  $k = 0$ , the two states  $\Gamma_1$  and  $\Gamma'_2$  arise from the two  $2s$  states, and each state has room for one electron each. The  $\Gamma'_{25}$  and  $\Gamma'_{15}$  are states which arise from the  $2p$  states of the atom, and each is triply degenerate, containing room for three electrons per atom. The symmetry of the state at  $k = 0$  in  $k$ -space is considerably different from the symmetry along either the (100) or (111) directions, so one expects that the mixture of the atomic-like states will change as one progresses away from the origin. In fact, such is the case, and the various  $s$  and  $p$  states become considerably mixed from the simple  $k = 0$  situation we have described. Of course, on a given curve, the degeneracy cannot change from the degeneracies we have quoted at  $k = 0$ , except where the curves cross.

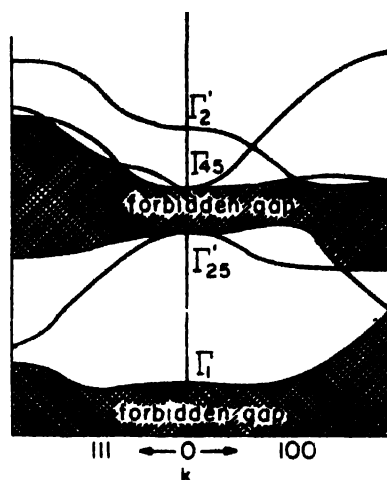


FIG. 7. The band structure of diamond  $E(k)$  is plotted in both the (100) and (111) directions of the crystal (H. Y. Fan).

We have cross-hatched what one would call the forbidden band in the figure. In this figure, we have only shown the energy as a function of  $k$  for two directions in  $k$ -space. Complete knowledge of the energy surfaces would include the region between these two directions; however, it is reasonable to suppose that the  $E(k)$  function in this unknown region holds no particular surprises.

There are several important features of the energy bands to be seen in this work. The first is that diamond is an insulator. The two lower curves supply just four energy states per atom, with a gap separating them from the upper valence band containing the remaining four states of the original atomic degenerate levels. An older work by Kimball<sup>11</sup> applied the cellular calculations to diamond, and shows how the splitting necessary to make diamond an insulator comes about. As the carbon atoms move closer together from a great distance, the  $s$  and  $p$  levels split and overlap. At a certain point, the lower states become a mixture of one  $2s$  and three  $2p$  states, just as we have seen in the detailed work of Herman and Slater and Koster. The second interesting feature of the work is that the "valence band" or first empty band does not have its minimum value at the origin

in  $k$ -space. From the point of view of the free electron approximation (see Eq. 33), this result is a little difficult to understand. In this connection, it has been known for some time that  $p$  bands are inverted. That is, the maximum energy of the band is at  $k = 0$  and the minimum energy is at  $k_{\max}$ . It is not difficult to understand this result from the tight binding discussion which we have already given.<sup>9</sup> However, in the case of diamond, the minimum is not in a special place along the (100) direction, but occurs somewhere between the minimum and maximum value of  $k$ .

The last point of interest in Fig. 7 is that the energy surfaces about the minimum point in the valence band need not be spherical. Indeed, in the similar case of Ge, the surfaces have a definite ellipsoidal character, and any electrons excited into the empty band have an effective mass which depends on their direction of propagation in  $k$ -space.

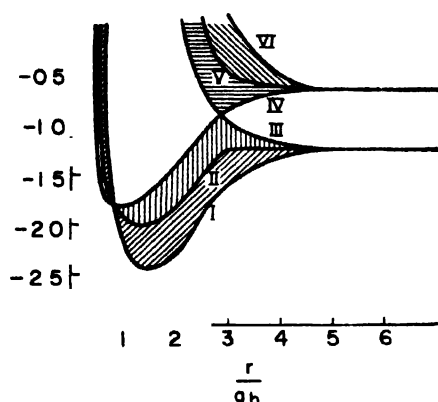


FIG. 8. The band separation in diamond, plotted as a function of lattice spacing. The figure shows how the  $s$  and  $p$  functions of the free atoms, which have room for 8 valence electrons, split apart for small lattice parameter into two groups. The lower group has room for just 4 electrons per atom (G. Kimball)

The general qualitative features of the diamond band structure are repeated in the cases of the other materials having diamond crystal structure. And in fact, this statement of similarity is true for all structures. Since the symmetry of the crystal is of supreme importance for the qualitative structure of the bands, it is found that as the potential function is changed by going to a different type of atom, only the magnitude of the band gaps, etc., are changed. For example, in the case of Ge, the forbidden band is very narrow compared to that of diamond, but otherwise the general picture of the bands is unchanged.

### 3.3.2 Ionic Crystals

The ionic crystals are made up of two or more different atoms, and the atoms of the crystal become nearly or completely ionized. Actually, the ionization of the constituent atoms of any crystal with more than one type of atom is more widespread than one generally realizes. For instance,

even in a metal alloy, there is some degree of ionization of the atoms, but the ionization does not proceed so far in this case as to destroy the essential metallic character of the mixture. In general, the good ionic crystals occur between elements which are far separated from each other in the electromotive series. Then the high chemical affinity of one of the constituent atoms for the valence electrons of the other overcomes the tendency of the mixture to become metallic.

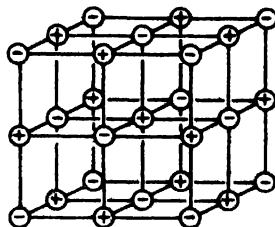


FIG. 9. The NaCl lattice  
(A. H. Cottrell).

NaCl is an almost perfect ionic crystal. It satisfies the condition concerning the relative chemical affinity of the two atoms. The binding force is simply the electrostatic force between the ions. A positive ion surrounds itself with nearest neighbors of the opposite charge, with other positive ions farther away, and the lattice constant is determined by the balance between the attractive coulomb force and the repulsive force of the closed shells of the ions. The band structure of NaCl is one of the simplest. It is obviously an insulator because the electrons are tightly bound to the ions, so there is a large gap between the highest filled band and the next (empty) band. It is in this type of material that the Heitler-London method has been applied with considerable success. The difficulty from the non-orthogonality of the wave functions on different atoms mentioned in the discussion of this method is not too bad in the case of the ionic crystals. The closed shells keep the overlap from becoming large because of the very sharp repulsion due to the Pauli principle. The Heitler-London method, of course, does not give the band structure, but does give the energy of the crystal, since one deals with the lowest energy wave function in this case. However, one can calculate the cohesive energy, compressibility and the lattice constants by this method.<sup>12</sup>

The band structure of several of the ionic crystals has been calculated by means of the cellular and tight binding approximations, with varying degrees of success.<sup>13</sup>

### 3.3.3 Metals

We have already outlined the results for the alkali metal, Na. One of the most interesting problems for the metals is to calculate the cohesive

energy from first principles, because the cohesive energy is so intimately related to the details of the wave function of the valence electrons.<sup>14</sup> Some degree of success has been attained for the simpler metals, but only after considerable labor. In addition to the calculation of the one-electron energies, it is necessary to include a correction due to the correlation forces. This correction is of course difficult to estimate, and is one of the more important reasons for the error when the calculated value is compared with the experimental one. The values of the cohesive energy for the metals are generally not as high as for the covalent and ionic crystals.

From many points of view, the most interesting metals are the transition metals, especially the ferro- or antiferromagnets. In the transition metals, the  $d$  and  $s$  shells are very close to one another in the free atoms, and a similar situation prevails in the crystalline solid. The band structures for all these metals are characterized by an overlap of the bands corresponding to the  $d$  and  $s$  atomic levels. All the evidence points to a relatively narrow and densely populated band due to the  $d$  electrons. Hence, these electrons do not contribute appreciably to the electrical conductivity of the metal because of their very high effective mass. The  $s$  band, on the other hand, is quite broad, with an electron mass approaching the free mass. The conduction electrons, then, are essentially the  $s$  electrons, but they are highly scattered by holes at the top of the  $d$  band, which fact leads to the relatively high resistivity of these metals. However, the  $d$  electrons do contribute to the cohesive energy in a positive way, and are responsible for the relatively high cohesive energy of metals like tungsten.

The ferromagnetic properties of the transition metals must still be labelled essentially not understood except in a very rough qualitative way. One of the early attempts<sup>15</sup> to understand the existence of ferromagnetism suggested that the Heitler-London method could be applied to the  $d$  shell because it was very narrow. However, this theory predicts that the spin moment per atom must be an integral number of Bohr magnetons. Actually, the moment is not integral, but is a fractional number of electron spins per atom. This result points to an intimate interaction between the  $s$  and  $d$  bands, and shows that some form of the Bloch theory must be applied to the  $s - d$  band mixture. So far, the complexity of the transition metals is great enough that the theory has not progressed very far.

### 3.3.4 *Molecular Crystals*

In the molecular crystal, molecules are bound together by the van der Waals force, leaving the electronic structure of the molecules essentially unchanged in the solid. The cohesive energy in this case is the weakest of



the four categories, being in the case of He only a fraction of an electron volt per atom. The very loose configuration of the molecular crystals does not split the molecular levels enough to form conventional bands, and the techniques we have been describing in this chapter are not necessary in this case.

#### 4. Correlation Problems

We have already pointed out how in the one-electron theory we have made a fundamental approximation which changes the character of the Schrödinger problem of the solid. We have assumed that the effective potential of an electron at any given point of the crystal is averaged over the motion of all the other electrons. This potential energy does not contain the instantaneous positions of the other electrons. This procedure was the most obvious way to separate the Schrödinger equation, and make it amenable to practical calculations. However, as we pointed out earlier, in doing this, we have replaced the many-body problem by a one-body problem.

Historically, there is one many-body problem which has been solved, albeit by numerical methods. This is the helium atom. The solution in this case has given a value of the energy which is in agreement with the experimental value of the ionization energy of He within the experimental accuracy of the measurement. The wave function obtained possesses a very strong correlation between the instantaneous positions of the electrons, which lowers the energy of the system by keeping the electrons separated from each other. That is to say, there is a "hole" in the charge distribution of the second electron in the immediate vicinity of the first. The primary result of any theory of the many body interaction must then be to introduce the correlation hole.

There is one type of correlation which is introduced into the wave function when the Pauli principle is imposed on the system by making the wave function a Slater determinant. Let us take two electrons (without spin) in the two lowest states in a one-dimensional box of unit length. Using the periodic boundary conditions, the wave function is

$$\Psi(1,2) = \frac{1}{\sqrt{2}} (e^{2\pi i x_1} - e^{2\pi i x_2}). \quad (41)$$

If we assume that one electron is at the origin, then the probability distribution of the other is given by

$$\Psi^*(x_1 = 0, x_2) \Psi(x_1 = 0, x_2) = 2 \sin^2 \pi x_2. \quad (42)$$

(42) shows that the probability distribution of the second electron is strongly peaked in the middle of the box. Hence the Pauli exclusion principle forces the second electron out of the vicinity of the first, and produces a "Fermi hole" in the wave function. This correlation has nothing to do with the Coulomb repulsion between the two electrons. Nevertheless, it does serve to lower the total energy of the system by reducing the average Coulomb energy between the two electrons over that of the simple product function,  $\Psi(1,2) = \psi(1)\psi(2)$ .

The result for the two electrons shows that if one electron is at the corner, the other essentially inhabits the middle of the "box." The three-dimensional,  $N$ -electron case is a little more complicated, but the results are still almost the same. Wigner and Seitz<sup>5</sup> showed, if one has  $N$  free electrons in a certain volume  $V$ , that the probability function for electron number 2 when electron 1 is at the origin, averaged over the wave functions of all the other electrons, has the same character. Namely, there is a volume around the first electron of size  $V/N$  within which a second electron is excluded, but its probability outside the volume rises asymptotically to a uniform value,  $1/V$ .

Obviously, with the introduction of the Pauli principle, we have come close to solving half the problem, because the Pauli principle digs its own hole which is not too far different from the hole which includes the Coulomb potential. At least the energy of the system with the Pauli hole is not far different from that with the correct wave function, although, of course, we do not in fact solve the  $n$ -body problem by simply including the Pauli correlation. However, for two electrons which have different spin, there is no Pauli principle correlation at all, and it is for this part of the problem that we need an estimate of the correlation energy.

#### 4.1 Perturbation Treatment

One might attempt the  $n$ -body problem by trying to use the results of the one-electron theory as the basis for a perturbation theory treatment with the interparticle Coulomb interaction as the perturbing Hamiltonian:

$$H' = \sum_{i,j} \frac{e_i e_j}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (43)$$

One would not offhand expect this perturbation to be a small one since the valence electrons are as close to each other as they are to the ions of the solid. However, as we shall see, there is a still more important failure. The perturbation theory has a peculiar divergence in second order.

Let us again treat the two free particles problem, because the results will provide us with insight into the  $n$ -particle problem. The three-dimensional lowest state Hartree-Fock wave function (again neglecting spin) for a cube of unit length is

$$\Psi_0(1,2) = \frac{1}{\sqrt{2}} (e^{i\mathbf{k}_1 \cdot \mathbf{x}_1} - e^{i\mathbf{k}_1 \cdot \mathbf{x}_2}); \quad (44)$$

$$k_x = 2\pi, \quad k_y = 0, \quad k_z = 0.$$

We shall now compute the perturbation to the energy of the system in the ground state in the second order. The first-order correction is straightforward and leads to the usual Coulomb and exchange energy terms. The second order energy correction is

$$E_2 = \sum \frac{|H'_{0n}|^2}{E_n} \quad (45)$$

in which  $H'_{0n}$  is the matrix element between the ground state (44) and the excited state,  $\Psi_n(1,2)$ :

$$H'_{0n} = \int d\mathbf{x}_1 d\mathbf{x}_2 \Psi_0^*(1,2) \frac{e^2}{|\mathbf{x}_1 - \mathbf{x}_2|} \Psi_n(1,2),$$

$$\Psi_n(1,2) = \frac{1}{\sqrt{2}} [\exp \{i(\mathbf{k}_1 \cdot \mathbf{x}_1 + \mathbf{k}_2 \cdot \mathbf{x}_2)\} - \exp \{i(\mathbf{k}_1 \cdot \mathbf{x}_2 + \mathbf{k}_2 \cdot \mathbf{x}_1)\}]. \quad (46)$$

The energy  $E_n$  of (45) is given by

$$E_n = \frac{\hbar^2}{2m} (k_1^2 + k_2^2). \quad (47)$$

We shall now compute the matrix element. When we make the change of variable  $\mathbf{x}_1 = (\mathbf{r}_1 + \mathbf{r}_2)/\sqrt{2}$  and  $\mathbf{x}_2 = (\mathbf{r}_2 - \mathbf{r}_1)/\sqrt{2}$ , we have

$$H'_{0n} = e^2 \int \frac{d\mathbf{r}_1 d\mathbf{r}_2}{|\mathbf{r}_1|} \left\{ \exp \left[ i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \frac{\mathbf{r}_1 + \mathbf{r}_2}{\sqrt{2}} + i\mathbf{k}_2 \cdot \frac{\mathbf{r}_2 - \mathbf{r}_1}{\sqrt{2}} \right] - \exp \left[ i\mathbf{k}_1 \cdot \frac{\mathbf{r}_1 + \mathbf{r}_2}{\sqrt{2}} + i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \frac{\mathbf{r}_2 - \mathbf{r}_1}{\sqrt{2}} \right] \right\}. \quad (48)$$

With the introduction of spherical coordinates in  $\mathbf{r}_1$  space, we have

$$H'_{0n} = 2\pi e^2 \int d\mathbf{r}_2 \exp(i\boldsymbol{\kappa} \cdot \mathbf{r}_2) \int \frac{dr_1}{r_1} r_1^2 dr_1 d(\cos \theta) [\exp(i\lambda r_1 \cos \theta) - \exp(i\gamma r_1 \cos \theta)],$$

$$\boldsymbol{\kappa} = (\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_1)/\sqrt{2}, \quad (49)$$

$$\lambda = |\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}_1|/\sqrt{2},$$

$$\gamma = |\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_1|/\sqrt{2}.$$

At this point, we shall manipulate our integrals as if the size of our box were infinite, even though we have normalized our wave functions to unit volume. The justification is that if a limit exists for the infinite integral, the integrals will be independent of the size of the box for a sufficiently large box. The integrals as they stand would be very difficult to do for a finite box, and would introduce surface effects which we would like to eliminate. We shall find, however, that the integrals are *not* independent of the size of the box, and shall return to the meaning of the results in a later paragraph.

The integration over  $d\mathbf{r}_2$  in (49) yields a delta function, and is the expression of the conservation of momentum. After integration over the angle  $\theta$ , we finally have

$$H'_{0n} = 32\pi^4 e^2 \delta(\mathbf{x}) \int d\mathbf{r} \left( \frac{\sin \lambda r}{r} - \frac{\sin \gamma r}{r} \right) \quad (50)$$

The integration in (50) is seen to be slightly pathological, but does possess a limit. If we multiply the integrand by  $e^{-\alpha r}$ , and take the limit  $\alpha \rightarrow 0$ , we obtain

$$H'_{0n} = 32\pi^4 e^2 \delta(\mathbf{x}) \left( \frac{1}{\lambda^2} - \frac{1}{\gamma^2} \right) \quad (51)$$

When we substitute this result in the formula for the second-order energy correction, we obtain, using the conservation of momentum,

$$E_2 \sim \int_{\mathbf{k}} d\mathbf{k} \frac{(2\mathbf{k}_i \cdot \mathbf{k}_1 - k_1^2)^2}{k_i^4 (\mathbf{k}_i - \mathbf{k}_1)^4 (k_i^2 - \mathbf{k}_i \cdot \mathbf{k}_1)} \quad (52)$$

This integral has a very bad singularity at the origin of  $\mathbf{k}$ -space, where the integral may be written as

$$\frac{1}{k_1} \int_0^{\infty} \frac{dk}{k^3} \quad (53)$$

The lower limit of integration in  $\mathbf{k}$ -space is of course finite for the finite box, because we are really performing a summation over the points of the reciprocal lattice in  $\mathbf{k}$ -space, and that summation is always a discrete and finite sum, not an integration. However, the lower limit is dependent on the *size of the box* in a very peculiar and unphysical way, and by taking the box large enough, we can make the contribution from this term as large

as we please. (Note that (52) is still correct for a box of any size even with proper normalization of the wave functions.) Essentially, we are involved in an infrared catastrophe. Due to the long range nature of the coulomb interaction, it is possible to run into trouble with scatterings between electrons which are far apart in which very small changes of momentum are involved. A similar difficulty arises in the solid when  $N$  electrons are put into the box. However, the singularity there is only logarithmic, instead of third power at the origin. This change is due to the fact that only a small fraction of the electrons can interact with small momentum transfers, namely those on the Fermi surface, and they must interact through intermediate states which satisfy the Pauli principle.

Physically, we know of course that no such singularity occurs in the energy of  $N$  electrons in a box, and something very basic is wrong with our description of the system. The thing which is wrong, of course, is that the electrons are not really free — we have not used a very sensible zero-order description of the  $n$ -particle system. Or, if we do use this description, great care must be used in summing the perturbation series with its singularities. There is an extreme sensitivity of the system to the motion of even one electron; that is, when we displace one electron from its initial position, the entire system reacts in a gross way due to the long range nature of the force field. We are thus reminded that the  $n$ -electron system is more like a bowl of jelly than a nebulous gas. A more qualitative description of the actual behavior of the  $n$ -electron system follows.

#### 4.2 Plasma Oscillations and Coulomb Screening

There are two important aspects of the electron gas which are rather surprising from the point of view of the free electron picture, and which are very difficult to demonstrate on that model. One is that the "rigidity" of the system due to the long range nature of the forces leads to a spectrum of oscillations which can be excited. These oscillations are entirely analogous to the oscillations which have already been observed for a long time in plasma discharges in evacuated tubes, and for this reason are called plasma oscillations in the case of the electrons also. The second, and for us the more important, property is that the electron gas does not actually behave, when an extra charge is introduced, as if every electron in the system interacts with the extra charge. Instead, the electrons in the immediate vicinity of the extra charge screen out the field of the charge, and the effective potential within the metal of the extra charge plus the polarization furnished by the neighboring charges amounts to a Yukawa-like screened coulomb field. There is of course nothing special about an extra charge, and the same

statement concerning the screening can be made about the electronic self-interaction itself, when the effects of the neighbouring electrons are accounted for. The screening and polarization effects are simply another way of describing the "Coulomb hole" we spoke of earlier.

These two properties of the electron gas are difficult to demonstrate in a rigorous way. Bohm and Pines<sup>3</sup> have adopted a treatment, which by means of a canonical transformation on the Hamiltonian and wave functions, brings in a set of variables which describe the collective motion of the system. The collective motion is just that which describes the way in which the entire system tends to react to a charge imbalance, and is responsible for the plasma oscillations. It is a beautiful feature of this treatment that a characteristic length comes up in a natural way, and corresponds to a breakdown in the collective mode of behaviour. In other words, at distances shorter than a characteristic length, the electrons behave like single particles, while at greater distances than this, the individual potentials of the electrons become screened out, and the system interacts in a more rigid or collective way.

An independent treatment of the problem is perhaps more attractive, but less physically pictorial, and is represented in the work of Gell-Mann and Bruckner.<sup>16</sup> This method is to adopt seriously the perturbation expansion point of view of the first part of this section, but to sum the perturbation series in a complete way and include all the higher order scattering processes which are important. It is accurate for high electron densities.

We shall adopt here a definitely less satisfactory, and less complete treatment than those quoted above. The reader is referred to the excellent review article by Pines in the "Solid State Physics" series<sup>17</sup> for further discussion, and, indeed, we shall use his point of view in the following.

Let us suppose that we have an electron gas and that the charge of the electrons is compensated by a uniform distribution of positive charge. On the average, the potential at any given point is zero. However, let us introduce an extra charge,  $q$ , at the origin and hold it fixed there. There is a redistribution in the electron distribution in the vicinity of the origin. Let us suppose that the number of electrons at any given point is given by the Fermi-Thomas solution, that is, the electron distribution is governed by statistical laws in the vicinity of the extra charge. In the presence of a potential which does not change appreciably over a space containing several electrons, we can write the local Fermi (kinetic) energy as equal to

$$E_t(\mathbf{x}) = E_t + eV(\mathbf{x}). \quad (54)$$

where  $E_t$  is the Fermi energy in a region where the potential  $V(\mathbf{x})$  is zero.

In writing (54), we have assumed that the *total* energy of an electron at the top of the Fermi distribution must be the same throughout the solid. Then, according to the formulas for free electrons in the first section of this chapter, we can write the local density of electrons as

$$n(\mathbf{x}) = \frac{[2m(E_f + eV(\mathbf{x}))]^{3/2}}{3\pi^2 \hbar^3} \quad (55)$$

The change in the electronic charge density due to the presence of the extra charge at the origin, and which causes the potential  $V$ , is then

$$e[n(\mathbf{x}) - n_0] = \frac{3}{2} \frac{n_0}{E_f} e^2 V. \quad (56)$$

We have calculated the local density in terms of the potential  $V(\mathbf{x})$ , which includes the potential of the charge at the origin and the additional potential due to the redistribution of the neighbouring electrons. On the other hand, classically, the potential is governed by the laws of electromagnetism, so we can write Poisson's equation for the potential  $V$ ,

$$\nabla^2 V(\mathbf{x}) = 4\pi q - 6\pi \frac{n_0}{E_f} e^2 V \quad (57)$$

The solution to this equation is

$$V(r) = \frac{q}{r} e^{-r/\lambda} \quad (58)$$

$$\lambda = \left( \frac{E_f}{6\pi n_0 e^2} \right)^{1/2}$$

The discussion we have just given is a modification to the Debye-Huckel theory of electrolytes, where we have used the Fermi statistics instead of Boltzmann statistics. However, the results are the same: we have found that the neighbouring electrons act to screen the effects of an additional charge held fixed at the origin. The screening length,  $\lambda$ , is the Debye length for the electrons and is a measure of the distance over which the individual potential of any one electron is noticeable. In the theory of Bohm and Pines, it forms the short wavelength limit of the plasma oscillations. Over distances larger than this length, the electrons behave collectively.

We shall now give a derivation of the frequency of the plasma oscillations, and show that the frequency corresponds to a larger energy than the Fermi energy. Hence the existence of the plasma oscillations is important only for outside excitations of the electrons; for example, these oscillations are excited by energetic bombarding particles, and can be observed as structure in the absorption spectrum for such particles.

Suppose that we take a slab of electrons and displace them rigidly a distance  $x$  perpendicular to the face of the slab. If the slab is also of thickness  $x$ , it is then attracted to the hole which is left with a force which is simply the force between two condenser plates, and we have

$$f = m\ddot{x} = -4\pi n_0 e^2 x. \quad (59)$$

The slab undergoes vibrations of frequency

$$\omega = \sqrt{4\pi n_0 e^2 / m}, \quad (60)$$

which is the plasma frequency. When the appropriate numbers are substituted in (60), the excitation energy of the first plasma excited state is found to be greater than the Fermi energy for all metals, which shows that a considerable energy is required to excite one of the plasma oscillations, and the ground state of the solid is undisturbed by them. Hence, from the viewpoint of the theory of the solid, the most important result of this work is the screening effect, which shows that one does not really have to worry about the long range nature of the force field and its resultant divergencies when calculating the wave function. When calculating the detailed electron-electron interaction in the solid, which we have averaged over in the electron theory of the last section, it is necessary only to use the screened coulomb interaction, which does in fact lead to a small correction term instead of the large one we feared earlier.

## 5. Lattice Vibrations

In the previous sections, we have either assumed that the underlying lattice was either a smoothly distributed positive charge (free electron theory), or that the atoms and ions were rigidly fixed in space on some sort of space lattice. However, the forces holding the lattice together are not capable of holding the atoms rigidly on their lattice, and indeed, we shall see that even when all possible vibration excitation is removed from the lattice, there is a zero-point residue related to the Heisenberg uncertainty principle.

The effective attractive forces between the atoms of a solid can arise in a multitude of ways, as we have already discussed. In an ionic crystal, they are the coulomb fields of the ions; in a metal, the cohesive force is due to the free electrons themselves; and in the covalent solid, the force is the covalent bond. When the atoms approach too close to one another, other forces, which are perhaps best described as due to the Pauli exclusion principle, come into play, and act to prevent the inner cores of atoms from



overlapping. The repulsive force is usually very sharp and of short range, while the attractive force is softer and longer ranging. Thus the potential energy of the crystal, plotted in the  $3N$ -dimensional configuration space of the crystal, is a generalized super Morse potential, with a minimum at the measured value of the lattice constant, where the repulsive and attractive forces balance each other.

Since the potential has a minimum value, we can expand it in a Taylor's expansion about the minimum, and the first nonzero terms in the expansion are quadratic. If we keep only the quadratic terms, the crystal becomes a system of harmonic oscillators, whose description we shall give in later paragraphs. However, we must remember that the higher terms in the expansion do exist, and are important for various reasons. Obviously they must *exist* in all solids, because there is no physical system in which the force is Hookean as the distance increases indefinitely. Hence, as the vibration amplitude increases, we can expect that the anharmonic terms will increase in importance. One of the properties of an oscillator with cubic terms in the potential is that the equilibrium position of the oscillator shifts as the amplitude changes. This phenomenon is the cause of the thermal expansion of a solid, and a measure of the thermal expansion gives a direct indication of the size of the neglected terms. It has even been suggested that the melting point of a solid might be due to the existence of a singularity in the mathematical solutions of the composite anharmonic oscillator. The anharmonic terms are also the cause of the heat conductivity of crystals, or rather of their resistivity, since without the anharmonic terms, the conductivity of insulators becomes very large.

In this section, we shall only derive the fundamental equations of the vibrating solid, and we refer the reader to the excellent works of Peierls,<sup>18</sup> and Born and Huang<sup>19</sup> for further discussion.

The most general quadratic expression for the potential energy of a crystal with atoms of equal mass,  $m_a$ , and one atom per unit cell is

$$V = \frac{1}{2} \sum_{i,j} \mathbf{x}_i \cdot \mathbf{A}_{ij} \cdot \mathbf{x}_j. \quad (61)$$

Here  $\mathbf{A}_{12}\mathbf{x}_1$  is the force vector on atom 2 when atom 1 is displaced a distance  $\mathbf{x}_1$ . By  $\mathbf{x}\mathbf{A}\mathbf{x}$  is meant the dot product between the second rank tensor  $\mathbf{A}$  and the two vectors  $\mathbf{x}$  and  $\mathbf{y}$ . This tensor product is then summed over all the atom pairs of the crystal.  $\mathbf{x}_i$  is the displacement in a cartesian coordinate system of the atom at lattice position  $i$ . Note that the indices  $i, j$  in (61) are not the tensor indices, which we have suppressed. The lattice point at

$i$  will also be called  $R_i$ , in accord with our earlier notation. The kinetic energy of the lattice is then

$$T = \frac{m_a}{2} \sum \dot{x}_i^2 \quad (62)$$

We shall now try to find the normal coordinates of the vibration problem. Our kinetic and potential energies are quadratic forms in the  $x$ 's and  $\dot{x}$ 's, and, according to a theorem,<sup>20</sup> they can both be diagonalized by the same coordinate transformation. The new coordinates are the normal coordinates of the system. Also, since the kinetic energy is already diagonalized, it will not change its form in the normal coordinate formulation, while the eigenvalues of the diagonalized potential energy are the frequencies of vibration. In the normal coordinate form, the kinetic and potential energies are then

$$T = \frac{1}{2} m_a \sum \dot{q}^2(\mathbf{k}),$$

$$V = \frac{1}{2} N m_a \sum_{\mathbf{k}} \omega^2(\mathbf{k}) q^2(\mathbf{k}). \quad (63)$$

The vector  $\mathbf{k}$  labels the normal coordinates as  $i$  did the original coordinates. There are  $3N$  of them. We shall try to solve the problem with a system of normal coordinates which are running waves in the lattice. Physically, this is a very reasonable solution, because we know that the meaning of the normal coordinate is that it is a mode of vibration in which the entire system vibrates with a fixed frequency, and a sound wave in a continuous medium is just such a mode. It is to be expected that the discrete lattice will not differ from the continuous one in the limit of long waves. The solution we try is

$$x_i = \sum_{\mathbf{k}, \lambda} q(\mathbf{k}, \lambda, t) e^{i\mathbf{k} \cdot \mathbf{R}_i},$$

$$q(k, \lambda, t) = q(\mathbf{k}, \lambda, t) e(\mathbf{k}, \lambda). \quad (64)$$

(64) is a general solution, and is made up of a superposition of the running waves  $e(\mathbf{k}, \lambda) e^{i\mathbf{k} \cdot \mathbf{R}_i}$ . The  $q(\mathbf{k}, \lambda, t)$  vector has the form  $e(\mathbf{k}, \lambda) q(\mathbf{k}, \lambda, t)$  and  $e$  is a unit vector which describes the polarization direction of the particular vibration mode. Note that we have introduced into (64) a new index,  $\lambda$ , separate from the  $\mathbf{k}$  vectors. The  $\lambda$  labels the polarization vectors. If we have an elastic wave  $\exp(i\mathbf{k} \cdot \mathbf{r})$  in a continuous solid, the polarization of

the wave is described by the decomposition of the wave with respect to three orthogonal unit vectors, two of which represent transverse waves, and one of which represents a longitudinal wave. Thus to a given value of  $\mathbf{k}$ , we have three degrees of freedom represented by the three different polarization possibilities. We assume that these results can be taken over into the solution of the normal coordinate problem. For a given  $\mathbf{k}$  vector, we assume there are three separate values of  $\lambda$  which correspond to three directions of polarization. For the moment, we shall not specify the directions of these vectors, but only assert there are three of them, and that they preserve the property of normal coordinates in that they are orthogonal to each other. In the continuous solid, the transverse waves have a different velocity than the longitudinal waves. The same will be true for the normal coordinates, and  $\omega(\mathbf{k})$  will in general be different for different  $\mathbf{e}$  vectors. Occasionally, when the meaning is obvious, we shall drop the index  $\lambda$  and the sum over the polarization vectors, and remember that in any sum over  $\mathbf{k}$ , each  $\mathbf{k}$  is threefold degenerate and that sums over  $\mathbf{k}$  are also sums over the different polarization vectors. We shall proceed by showing that the choice of solution, (64) does indeed diagonalize the potential energy without changing the form of the kinetic energy

Before going further with our discussion of the diagonalization, however, we need a result concerning lattice sums which is called the completeness relation. The theorem is

$$\sum_{\mathbf{R}_j} e^{i\mathbf{k} \cdot \mathbf{R}_j} = N\delta_{\mathbf{k}, \mathbf{K}}. \quad (65)$$

The sum is over all the lattice points,  $\mathbf{R}_j$ , and the  $\mathbf{k}$  vectors are the  $\mathbf{k}$  vectors of the Born von Kármán boundary conditions. Suppose we displace the crystal by a lattice vector,  $\mathbf{R}_i$ . Then the entire sum is multiplied by the term  $e^{i\mathbf{k} \cdot \mathbf{R}_i}$ . On the other hand, the sum is not really changed, since we have only relabelled the lattice sites by our displacement. Hence, the sum must either be zero, or the phase  $\mathbf{k} \cdot \mathbf{R}_i$  must be a multiple of  $2\pi$ , that is,  $\mathbf{k}$  must be a reciprocal lattice vector,  $\mathbf{K}$ . On the other hand, if  $\mathbf{k}$  is such a reciprocal lattice vector, the sum yields the number of lattice points,  $N$ . The reader will note the similarity of (65) to the Fourier representation of the delta function.

At this point, we shall take notice of another fundamental relationship. We have already said that the normal coordinates should correspond to the sound waves in a continuous medium. Hence the usual boundary conditions at the surface should still be satisfied by our normal coordinate vibrations. We shall again use the Born-von Kármán boundary conditions, and require

that the waves repeat themselves with a fundamental cube which contains  $N$  atoms. This requirement is exactly the same one that we have seen before for the  $\mathbf{k}$  vectors of the Bloch functions, and the allowed  $\mathbf{k}$  vectors of the Bloch functions are precisely the same ones which we shall use for our normal coordinates. We also said that the number of  $\mathbf{k}$  vectors in the first  $B$ -zone of  $\mathbf{k}$  space is just equal to the number of atoms,  $N$ . Since we must have only as many normal coordinates as we had original coordinates,  $\mathbf{x}_i$ , whose number is  $3N$ , we have in the first  $B$ -zone a very convenient choice for the region of  $\mathbf{k}$ -space we shall allow in picking the normal coordinates of the system. (We have assumed that for each vector  $\mathbf{k}$ , there are 3 separate polarization directions so that the total number of normal modes is the required  $3N$ .) There is just one reciprocal lattice vector in the first zone, namely the origin. Hence in (65), the Kronecker delta should be written  $\delta_{\mathbf{k},0}$  or  $k = 0$ , and (65) becomes

$$\sum_{\mathbf{R}_j} e^{i\mathbf{k} \cdot \mathbf{R}_j} = N\delta_{\mathbf{k},0}. \quad (66)$$

We can now write the kinetic energy as

$$T = \frac{1}{2} m_a \sum_j \sum_{\mathbf{k}, \mathbf{k}'} \dot{\mathbf{q}}(\mathbf{k}, t) \cdot \dot{\mathbf{q}}(\mathbf{k}', t) \exp [i\mathbf{R}_j \cdot (\mathbf{k} + \mathbf{k}')]. \quad (67)$$

With the help of (66), the sum over the index ( $j$ ) can be carried out, and

$$T = \frac{Nm_a}{2} \sum_{\mathbf{k}} \dot{\mathbf{q}}^*(\mathbf{k}, t) \cdot \dot{\mathbf{q}}(\mathbf{k}, t), \quad (68)$$

which shows that the kinetic energy is still diagonal. In (68), we have used the fact that  $q^*(\mathbf{k}, t) = q(-\mathbf{k}, t)$ , which we know because in (64),  $\mathbf{x}_i$  is real. The summation over the polarization indices,  $\lambda$ , in (67) leads to no cross terms in (68), because of the assumed orthogonality of the three polarization vectors for a given  $\mathbf{k}$ .

The potential energy becomes

$$V = \frac{1}{2} \sum_{i,j} \sum_{\mathbf{k}, \mathbf{k}'} q(\mathbf{k}, t) A_{ij} q(\mathbf{k}', t) \exp [i(\mathbf{k} \cdot \mathbf{R}_i + \mathbf{k}' \cdot \mathbf{R}_j)]. \quad (69)$$

In this expression, we have the matrix

$$\sum_{i,j} A_{ij} \exp [i(\mathbf{k} \cdot \mathbf{R}_i + \mathbf{k}' \cdot \mathbf{R}_j)]. \quad (70)$$

This double sum can be simplified by realizing that the force tensor or matrix,  $A_{ij}$ , is invariant under a primitive translation of the lattice. That is,  $A_{ij}$  is only a function of the relative distance between two atoms, because all the atoms of the crystal are equivalent. The sum over all the pairs of the crystal, (70), then, can be written in the form of a sum over the lattice, ( $i$ ), and a second sum over the difference vectors of the lattice, ( $\mathbf{R}_l = \mathbf{R}_j - \mathbf{R}_i$ ).

$$\begin{aligned} & \sum_{i,l} A_l \exp [i(\mathbf{R}_l + \mathbf{R}_i) \cdot \mathbf{k}' + i\mathbf{R}_i \cdot \mathbf{k}] \\ &= \sum_l A_l \exp (i\mathbf{R}_l \cdot \mathbf{k}') \left\{ \sum_i \exp [i\mathbf{R}_i \cdot (\mathbf{k}' + \mathbf{k})] \right\} = N \delta_{\mathbf{k}' + \mathbf{k}, 0} \sum_l A_l \exp (i\mathbf{k}' \cdot \mathbf{R}_l). \end{aligned} \quad (71)$$

The potential energy now becomes

$$V = \frac{1}{2} N \sum_{\mathbf{k}, \lambda} \left\{ \mathbf{e}(\mathbf{k}, \lambda) \left[ \sum_l A_l \exp (i\mathbf{k} \cdot \mathbf{R}_l) \right] \mathbf{e}(\mathbf{k}, \lambda) \right\} |\mathbf{q}(\mathbf{k}, \lambda, t)|^2. \quad (72)$$

Except for the quantity in the braces, the potential energy is diagonalized. However, the matrix  $A$  mixes up the polarization vectors together, and (72) is not a simple sum of squares so far as the polarization vectors are concerned. We can remedy the situation, however, by carrying out a separate diagonalization process, for each vector  $\mathbf{k}$ , of the quadratic form in the braces. Or, the problem can be written in the slightly more familiar eigenvector form

$$\left( \sum_l A_l \exp (-i\mathbf{k} \cdot \mathbf{R}_l) \right) \mathbf{e}(\mathbf{k}, \lambda) = \frac{\omega^2(\mathbf{k}, \lambda)}{N} \mathbf{e}(\mathbf{k}, \lambda). \quad (73)$$

The eigenvector solutions,  $\mathbf{e}(\mathbf{k}, \lambda)$ , determine the directions of the polarization vectors which we left unspecified in (64); and the eigenvalues,  $\omega(\mathbf{k}, \lambda)$ , are the frequencies of the normal coordinates. The rank of the matrix  $A$ , is 3, and the eigenvalues for a given  $\mathbf{k}$  are the solutions of the determinant

$$\left[ \sum_l A_l \exp (i\mathbf{k} \cdot \mathbf{R}_l) - U \frac{\omega^2(\mathbf{k})}{N} \right] = 0. \quad (74)$$

$U$  is the unit matrix. There are just three solutions, corresponding to the three independent polarization directions possible. Since the eigenvector solutions of (73) are orthogonal to one another, we see that our assumption that three mutually orthogonal polarization vectors exist for each  $\mathbf{k}$  is consistent. Two of the waves will be transverse, and one will be longitudinal for long waves, although we shall not prove this statement.

In order to be complete, we shall note the time dependence of  $q(\mathbf{k}, t)$ . Suppose that we only excite one of the normal vibrations for a given  $k$ . Then the total energy is

$$T + V = \frac{Nm_a}{2} (|\dot{q}|^2 + \omega^2 |q|^2). \quad (75)$$

This is the energy of a single harmonic oscillator, and

$$q = \alpha e^{i\omega t}. \quad (76)$$

### 5.1 Phonons

Our discussion thus far in this section has been classical. We shall, however, want to quantize the oscillators of the solid, and we do it by making the usual commutator between the momentum and position coordinates. First we show how to write the Hamiltonian of the system. The total energy is

$$T + V = Nm_a \sum (|\dot{q}(\mathbf{k})|^2 + \omega^2(\mathbf{k}) |q(\mathbf{k})|^2). \quad (77)$$

Hence, we see that the momentum of one of the oscillators is simply

$$\mathbf{p}(\mathbf{k}) = Nm_a \dot{q}(\mathbf{k}) = M \dot{q}(\mathbf{k}). \quad (78)$$

$M$  is the total mass of the solid. From this last equation, we have the Hamiltonian operator

$$H = \sum_{\mathbf{k}} \left\{ \frac{1}{2M} |\mathbf{p}(\mathbf{k})|^2 + \frac{M\omega^2(\mathbf{k})}{2} |q(\mathbf{k})|^2 \right\} \quad (79)$$

The commutator between the operators  $p_x$  and  $q_x$  is, as always,

$$[p_x(\mathbf{k}), q_x(\mathbf{k}')] = \frac{\hbar}{i} \delta_{\mathbf{k}, \mathbf{k}'}. \quad (80)$$

There are several ways to solve the quantum mechanical problem. We could write down the Schrödinger equation for the Hamiltonian we have given, and obtain the usual Hermite polynomial solution. However, there is a more elegant method, a method which gives us immediately the matrices for  $q(\mathbf{k})$ , which we shall need later. We introduce the so-called creation and destruction operators for a given  $(\lambda, \mathbf{k})$ ,  $a(\mathbf{k})$  and  $a^\dagger(\mathbf{k})$ , by the equations

$$\begin{aligned} p(\mathbf{k}) &= \sqrt{\frac{\hbar M \omega}{2}} (a^\dagger(\mathbf{k}) - a(\mathbf{k})), & |p|^2 &= p^\dagger p, \\ q(\mathbf{k}) &= \sqrt{\frac{\hbar}{2M \omega}} (a^\dagger(\mathbf{k}) + a(\mathbf{k})), & |q|^2 &= q q^\dagger \end{aligned} \quad (81)$$

The operators  $p$  and  $q$  have the proper commutator if the  $a$ -operators satisfy the following commutation relations

$$\begin{aligned} [a(\mathbf{k}), a(\mathbf{k})] &= [a^\dagger(\mathbf{k}), a^\dagger(\mathbf{k})] = 0, \\ [a(\mathbf{k}), a^\dagger(\mathbf{k})] &= 1. \end{aligned} \quad (82)$$

All pairs of  $a$ -operators are assumed to commute if they are associated with different values of  $\mathbf{k}$ . A matrix representation for the  $a$ -operators, which satisfies the commutation relations, is

$$\begin{aligned} a &= \begin{vmatrix} 0 & 1 & 0 & 0 & \dots \\ 0 & 0 & \sqrt{2} & 0 & \dots \\ 0 & 0 & 0 & \sqrt{3} & \dots \\ \vdots & & & & \end{vmatrix} & a^\dagger &= \begin{vmatrix} 0 & 0 & 0 & 0 & \dots \\ 1 & 0 & 0 & 0 & \dots \\ 0 & \sqrt{2} & 0 & 0 & \dots \\ \vdots & & & & \end{vmatrix} \\ a^\dagger a &= 1 + aa^\dagger = \begin{vmatrix} 1 & & & & \\ & 2 & & & \\ & & 3 & & \\ 0 & & & & \\ & & & & \end{vmatrix}. \end{aligned} \quad (83)$$

In terms of the  $a$ -operators, the Hamiltonian becomes simply

$$H = \frac{\hbar}{2} \sum_{\mathbf{k}} \omega(\mathbf{k}) (a^\dagger(\mathbf{k})a(\mathbf{k}) + a(\mathbf{k})a^\dagger(\mathbf{k})), \quad (84)$$

and when reference is made to the matrices of (83), we see that the Hamiltonian is diagonal. The energy eigenvalues of the system are simply

$$E = \sum \hbar\omega(\mathbf{k}) (n(\mathbf{k}) + \frac{1}{2}). \quad (85)$$

Here,  $n(\mathbf{k})$  is the quantum number associated with the oscillator  $\mathbf{k}$ , and is a positive integer or zero. In order to obtain the total energy, we have summed over all the oscillators. The  $\frac{1}{2}$  is the zero-point energy of vibration, which in the case of the lattice vibrations is real and detectable. It assures us that the Heisenberg uncertainty relations are satisfied for the atoms of the lattice.

There is a very widely used interpretation of the equations we have just written. The quantized equations for the sound wave vibrations of the solid are very similar to the quantized electromagnetic equations. The electromagnetic equations on the other hand, lead to the concept of particle

photons. Our Eq. (85) can be interpreted in the same way. We can say that each quantum of excitation possessed by a particular oscillator is a kind of particle, because we see that the energy of the oscillator in excess of the zero-point energy is just  $n(\mathbf{k})$  (the number of particles) times  $\hbar\omega(\mathbf{k})$  which is the quantum of energy of each particle. We call these particles phonons by analogy to the photon case.

The  $a$ -matrices are called creation and destruction operators, because when they operate on a given state vector,  $a(\mathbf{k})$  increases the number of phonons in the oscillator  $\mathbf{k}$  by one, and  $a^\dagger(\mathbf{k})$  decreases it by one. Thus they create or destroy one phonon of a given  $\mathbf{k}$  vector at a time.

Before leaving this section on lattice vibrations, we shall make a comment on the zero-point vibrations of the solid. We have stated that they are real. They are, in principle, perfectly detectable to an X-ray machine or to neutrons which can be used to compute the lattice constant at absolute zero temperature. On the other hand, the zero-point vibrations of the solid do not constitute scattering agents for the electrons of the solid at absolute zero. We have seen how the Bloch theorem leads to the concept of an electron running through a crystal with no interference with the lattice if the lattice is rigidly fixed in space. The Bloch theorem should be expected to break down when the lattice atoms are allowed to move. However, we will show in the next section that the zero-point motion of the lattice is, from the point of view of Bloch's theorem, no motion at all!

## 5.2 Thermal Behaviour

If we use the particle terminology for the normal modes, then we must indicate how to deal with the many-particle system in a statistical way. Since there is no restriction to the number of phonons in a given oscillator (see Eq. 85), the phonon system satisfies the Bose-Einstein statistics. Hence the number of phonons in a given oscillator mode  $\mathbf{k}$  at the temperature,  $T$ , is given by

$$n(\mathbf{k}) = \frac{1}{e^{\hbar\omega/kT} - 1} \quad (86)$$

The thermal properties of the phonon system are quite complicated because we do not know the function  $\omega(\mathbf{k})$ . To find it, one would have to solve the eigenvalue problem (83), which for the three-dimensional crystal is very difficult. A related quantity to the function  $\omega(\mathbf{k})$  is the density of states curve, i.e., the number of  $\mathbf{k}$  states corresponding to a given value



of the frequency. Some numerical attempts have been made on simplified models to compute the density of states curve, and the density of states turns out to be quite complicated. However, a much more primitive procedure due to Debye is usually used to describe the situation. Debye suggested that the function  $\omega(\mathbf{k})$  might be approximated by the continuum elastic value. Thus there should be two transverse and one longitudinal modes, and the two types of modes should be characterized by their separate sound velocities. He assumed these velocities were constant over the entire frequency range and that the crystal was elastically isotropic so the velocity does not vary with direction. If we neglect the fact that the longitudinal and transverse sound wave velocities are different, we have that  $\omega = ck$ . With this assumption of  $\omega(\mathbf{k})$ , we can find the highest frequency since we can find the maximum  $\mathbf{k}$  vector by requiring that the number of points in  $\mathbf{k}$ -space enclosed by a sphere with  $k = k_{\max}$  is equal to  $N$ . (There are  $3N$  degrees of freedom, but also 3 polarization directions for each  $\mathbf{k}$  vector.)

$$N = \frac{L^3}{6\pi^2} k_{\max}^3 = \frac{L^3}{6\pi^2} \frac{\omega_{\max}^3}{c^3}. \quad (87)$$

With this approximation, Debye was able to give a theory of the specific heat of the lattice which has many of the observed experimental features. The calculation is feasible because now one has a way of deriving the density of states for a given energy, and from this the average energy of the crystal follows. We refer the reader to other books for a discussion of the results. However, it will be important for us to define a parameter which is useful whenever lattice effects are important. We note that the maximum frequency of (87) can be expressed in terms of an energy, and this energy also has an equivalent temperature. This temperature is the Debye  $\theta$ , or the Debye temperature.

$$\frac{\hbar\omega_{\max}}{k} = \theta. \quad (88)$$

In this formula,  $k$  is Boltzmann's constant. The physical importance of the parameter  $\theta$  is that it represents the dividing line between the low temperature and high temperature effects. At temperatures well below the Debye temperature, we can expect quantum effects to be important, while at higher temperatures, the thermal energy is sufficient to excite all the modes of vibration, and the phonons should be distributed approximately according to the classical Boltzmann statistics. Above this temperature, then, the specific heat of the lattice approaches its classical value of  $3R$  per mole for a monatomic crystal.

## 6. Electron-Lattice Interactions

We have already indicated the possible importance of the motions of the lattice atoms on the electronic structure. As we mentioned in the introduction, we deal in this case with the breakdown of the broad division of our study of the solid into electrons and lattice. We have shown in the previous sections how the electronic structure can be studied separately, with a view to such things as the cohesive energy and band structure. On the other hand, there are also specific lattice effects. One of these is the specific heat of the crystal due to the thermal motion of the lattice atoms. It is also possible to discuss certain types of lattice defects with only a cursory mention of the existence of the underlying electronic structure. Examples are the diffusion in solids and the mechanical properties of crystals. When, as we shall do now, we begin to discuss how the lattice motion disturbs the electronic structure, we can expect the subject to be intrinsically more difficult than the previous topics, and our models of the solid often have to be extremely simplified. However, on the other hand, one of the most important recent advances in the theory of solids is the explanation of the superconductivity of certain metals on the basis of the electron-lattice interaction, so it is possible to construct quite adequate and even quantitative theories in this field.

In both the metal and the ionic crystals, the interaction between the electrons and the lattice vibrations is large enough so that a straightforward application of the perturbation theory leads to questionable results. In the ionic crystals, the interaction is large because the ions of the crystal are charged, and the motion of the charged ions is able to have large effects on any free electrons present. In the case of the metal, the interaction is large for the reason that the ions of the metal are held together by the rather nebulous sea of quasi-free electrons surrounding them, and any motion of the ions of the lattice tends to upset the delicate electronic states. In fact, Wentzel<sup>21</sup> has shown that the simple electron-lattice interaction is so strong that a one-dimensional lattice of atoms with free electrons is unstable and will collapse. Specifically, he shows that one can solve exactly the problem of the electrons interacting with the phonon system with any strength of the interaction constant, and that the size of the interaction constant in a metal is indeed in the unstable region. Peierls<sup>18</sup> has suggested that this tendency for the lattice to be unstable is connected with the experimental fact that the metals are found with generally rather complicated crystal structures when compared with the other solids. That is, the balance between the ion motion and the electronic structure is rather delicate and can lead to lattice structures which are not close packed.

Of course, the true metal is not unstable, and the reason is the added coulomb interaction between the electrons, which we have already discussed. Bardeen *et al.* have noted<sup>82</sup> that these two interactions are of about the same amount but of different sign. The lattice interaction essentially is an attractive one between the electrons because it decreases the energy of the system, while the coulomb interaction is of course repulsive, and keeps the lattice from collapsing. Indeed, Bardeen *et al.* have shown that it is the relative sizes of these "self-energies" for a given lattice which determines whether the electrons gang up with the phonons to create the superconducting state, or whether the coulomb energy keeps them separated and in the normal Fermi distribution.

### 6.1 Metallic Conductivity

As an example of the effect of the lattice motion on the electronic structure, we shall now turn to one of the oldest problems in the theory of metals, namely, the explanation of the temperature dependent part of the resistivity of the metal. In fact, Lorentz in the 19th century gave a classical theory of the resistivity which bears considerable similarity in general outline to the quantum theory which we shall present.

We have stated before that the resistance of a metal is caused by the scattering of the electrons by the phonons of the lattice. However, if our discussion is to be quantitative, we must calculate how the distribution of electrons in  $\mathbf{k}$ -space is disturbed, in the first place by the application of the electric field, and in the second place by the interaction between the excited electrons and the elastic vibrations. The problem is then in reality simply one of kinetic theory, and we find ourselves discussing the quantum equivalent of Boltzmann's transport equation familiar in the kinetic theory of gases.

Consider a wire of metal with an external electric field,  $F$ , in the  $z$ -direction, and a net current of electrons down the wire. In the normal Fermi distribution, the number of electrons going in one direction is exactly balanced by the electrons going in the opposite direction. However, the effect of the field is to shift the whole distribution rigidly in  $\mathbf{k}$ -space until the extra collisions suffered by the unbalanced portion of the electrons cancels the tendency of the field to shift the distribution to higher and higher values of net current. We can express the new state of equilibrium by means of the equation

$$\left( \frac{\partial f(\mathbf{k})}{\partial t} \right)_F + \left( \frac{\partial f(\mathbf{k})}{\partial t} \right)_{\text{coll}} = 0. \quad (89)$$

Here, we require that the density of electrons,  $f(\mathbf{k}, t)$  for a given quantum state  $\mathbf{k}$  is a constant in time, so that the number of transitions into the state is cancelled by the number of transitions out of the state.  $(\partial f / \partial t)_F$  is the change in the occupation number of the state due to the acceleration of the electrons in the field, and  $(\partial f / \partial t)_{\text{coll}}$  is the change in the occupation number due to the collisions with the lattice vibrations.

The change in the electron density function,  $f(\mathbf{k})$ , due to the acceleration in the field is the easiest half of the problem. We can make this calculation very directly with the use of the Dirac density matrix. The total one-electron  $\psi$  function for the  $j$ th electron can be expressed in terms of the complete set of Bloch waves by means of

$$\psi_j(\mathbf{x}, t) = \sum \alpha_j(\mathbf{k}, t) \psi_{\mathbf{k}}(\mathbf{x}, t). \quad (90)$$

(Note the difference between the present definition and 11.) We shall restrict ourselves to the wave functions of a single band. The density matrix,  $\rho_{\mathbf{k}, \mathbf{k}'}$  is then defined in terms of the expansion coefficients,  $\alpha_j$ , by

$$\rho_{\mathbf{k}, \mathbf{k}'} = \sum \alpha_j^*(\mathbf{k}', t) \alpha_j(\mathbf{k}, t). \quad (91)$$

The Heisenberg equation of motion for the density matrix is

$$\dot{\rho} = \frac{i}{\hbar} [\rho, H]. \quad (92)$$

The Hamiltonian in this equation is made up of two parts. (So far we are not including the interaction with the phonon field.) It contains the complete periodic crystal Hamiltonian,  $H_p$ , which leads to stationary solutions in terms of the Bloch waves. The time dependence is contributed by that part of the Hamiltonian due to the electric field,  $-eFz$ .

$$H = H_p - eFz. \quad (93)$$

Hence, we have

$$\dot{\rho} = -\frac{ieF}{\hbar} [\rho, z]. \quad (94)$$

In order to proceed further, we need to find an expression for the matrix of  $z$ . For the sake of a simple calculation, we shall assume that the Bloch

wave functions are the free electron wave functions, so the matrix of  $(z)$  takes the form

$$\begin{aligned} z_{k'k} &= \int d\mathbf{x} z e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{x}} \\ &= -i \frac{\partial}{\partial k_x} \int e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{x}} d\mathbf{x} \\ &= -i \frac{\partial}{\partial k_x} \delta(\mathbf{k} - \mathbf{k}'). \end{aligned} \quad (95)$$

(The results we shall obtain for the plane wave solutions are still valid for the more general Bloch functions, but are somewhat more awkward to derive.) When we make the substitution of  $(z)_{kk'}$  into (94) and perform the matrix multiplication by summing (integrating) over the index  $k''$ , we find

$$\begin{aligned} \dot{\rho}_{k'k} &= -\frac{eF}{\hbar} \sum_j \int d\mathbf{k}'' \left[ \alpha_j^*(\mathbf{k}') \alpha_j(\mathbf{k}'') \frac{\partial}{\partial k_x} \delta(\mathbf{k} - \mathbf{k}'') + \alpha_j^*(\mathbf{k}'') \alpha_j(\mathbf{k}) \frac{\partial}{\partial k_x} \delta(\mathbf{k}' - \mathbf{k}'') \right] \\ \dot{\rho}_{k'k} &= -\frac{eF}{\hbar} \sum_j \left[ \alpha_j^*(\mathbf{k}') \frac{\partial}{\partial k_x} \alpha_j(\mathbf{k}) + \frac{\partial \alpha_j^*(\mathbf{k}')}{\partial k_x} \alpha_j(\mathbf{k}) \right]. \end{aligned} \quad (96)$$

Since the diagonal elements of the density matrix have the meaning of the occupation number of the corresponding states, we have that

$$\begin{aligned} \dot{\rho}_{kk} &= -\frac{eF}{\hbar} \frac{\partial}{\partial k_x} \rho_{kk}, \\ \left( \frac{\partial f(\mathbf{k})}{\partial t} \right)_F &= -\frac{eF}{\hbar} \frac{\partial f(\mathbf{k})}{\partial k_x}. \end{aligned} \quad (97)$$

This last equation is identical to one we might have derived for the more general Bloch functions, and it is also identical to the classical result calculated on the basis of Liouville's theorem by Boltzmann.<sup>23</sup>

## 6.2 Electron-Phonon Collisions

In the second part of the problem, we have to calculate the rate of change of the density function due to the collisions with the phonons. For this purpose, we can use the familiar formula from first order time dependent perturbation theory (Vol. I, Chapter 8, § 5.1.1) for the rate of transition from state 1 to state 2.

$$T_{1 \rightarrow 2} = \frac{2\pi}{\hbar} |H'_{12}|^2 \delta(E_1 - E_2). \quad (98)$$

We apply (98) to the Bloch one-electron wave function  $\psi_e(\mathbf{k})$ , and since we are calculating the interaction between the lattice and electrons, we must also include the wave function of the lattice. Hence the matrix element is

$$H'_{12} = \int \psi_{e_1}^* \psi_{e_2}^* H' \psi_{e_1} \psi_{e_2} d\mathbf{x} \quad (99)$$

$\psi_e$  is the wave function of the crystal which we discussed in section 5.  $H'$  is the interaction Hamiltonian.

The interaction Hamiltonian,  $H'$ , which causes an electron to be scattered from one  $\mathbf{k}$  vector to another is simply the difference between the perfectly periodic lattice potential and the potential when the ions of the crystal are shifted by various amounts. If we expand the potential function of the non-periodic lattice with a Taylor's series which contains the perfect lattice as the zero-order term, we have

$$V(\mathbf{x}) = \sum_{\mathbf{R}_j} [V_0(\mathbf{x} - \mathbf{R}_j) + \mathbf{x}_j \cdot \mathbf{W}(\mathbf{x} - \mathbf{R}_j)], \quad (100)$$

$$H' = \sum \mathbf{x}_j \cdot \mathbf{W}(\mathbf{x} - \mathbf{R}_j)$$

$\mathbf{W}(\mathbf{x} - \mathbf{R}_j)$  is the gradient of the potential,  $V_0(\mathbf{x})$ , evaluated at the position of the cell  $\mathbf{R}_j$ . Since  $V_0(\mathbf{x})$  is periodic, the function  $\mathbf{W}(\mathbf{x} - \mathbf{R}_j)$  is also periodic. The term  $\mathbf{x}_j$  is the displacement of the atom in the cell at  $\mathbf{R}_j$ . We have, as always, assumed only one atom per cell for the sake of the simplicity of our formulas. Hence, (100) becomes a sum of products between one function,  $\mathbf{W}$ , which is a function of the electron coordinates, and another function,  $\mathbf{x}_j$ , of the lattice coordinates. The total matrix element is then simply the sum of a set of products of the matrices  $\mathbf{W}$  in the electron Hilbert space with the matrices  $\mathbf{x}$  in the lattice Hilbert space. (These products are the so-called outer matrix products, and are *not* ordinary matrix multiplication or inner matrix products.) When we decompose the lattice into normal modes, we find, according to (64)

$$H' = \sum \sum q(\mathbf{x}, t) e^{i' \cdot \mathbf{R}_j} \mathbf{e}(\mathbf{x}) \cdot \mathbf{W}(\mathbf{x} - \mathbf{R}_j). \quad (101)$$

We remember from (81) and (83) that the matrix  $q$  has matrix elements for each mode of vibration in which the number of phonons in each mode,  $n(\mathbf{x})$ , is increased or decreased by one. The matrix element is proportional to

$\sqrt{n(\mathbf{x}) + 1}$  or  $\sqrt{n(\mathbf{x})}$ , respectively, when the number of phonons is increased or decreased.

In (101), we have a lattice sum,

$$\sum e^{i\mathbf{x} \cdot \mathbf{R}_j} W(\mathbf{x} - \mathbf{R}_j), \quad (102)$$

which can be simplified. The matrix  $W$  is written

$$\{W(\mathbf{x} - \mathbf{R}_j)\}_{k_1 k_2} = \int d\mathbf{x}_0 \psi_{k_1}^*(\mathbf{x}) W(\mathbf{x} - \mathbf{R}_j) \psi_{k_2}(\mathbf{x}). \quad (103)$$

The integration here is over the cell  $\mathbf{R}_j$ . Because of the periodicity of the potential and Bloch's theorem, we can write (103) as an integral over the cell at the origin. Then the lattice sum, (102), becomes

$$\sum_{\mathbf{R}_j} \exp [i(\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{x}) \cdot \mathbf{R}_j] \int d\mathbf{x}_0 \psi_{k_1}^*(\mathbf{x} - \mathbf{R}_j) W(\mathbf{x} - \mathbf{R}_j) \psi_{k_2}(\mathbf{x} - \mathbf{R}_j).$$

With the use of the completeness relations, (65), the lattice sum becomes

$$(W)_{k_1 k_2} N \delta(\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{x}, \mathbf{K}). \quad (104)$$

This expression contains the statement of the conservation of the wave vector when the electron is scattered,

$$\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{x} = \mathbf{K}. \quad (105)$$

In the formula (101), we still have the sum over the modes of vibration  $\mathbf{x}$ . Because of the necessity to conserve both energy and wave vector or momentum, it will not be possible to scatter the electron from a given state into a completely arbitrary state. In fact, the scattering becomes very complicated for the general case because one does not usually know  $\omega(\mathbf{x})$  sufficiently accurately. However, there will be two separate cases. It will in general be possible to find a final state  $\mathbf{k}_2$  in which one phonon of the mode  $\mathbf{x}$  is destroyed, and another final state  $\mathbf{k}_2'$  in which a phonon of a different mode is created. We can write the rate of transition into each of these final states, after making use of the value (81) for  $q(\mathbf{x})$ , in the following way

Creation:

$$\begin{aligned} T_{1 \rightarrow 2} &= \frac{\pi}{m_a} \frac{n(\mathbf{x})}{\omega(\mathbf{x})} |(k_1|W|k_2)|^2, \\ E_{k_1} &= E_{k_2} + \hbar\omega(\mathbf{x}), \\ \mathbf{k}_1 - (\mathbf{k}_2 + \mathbf{x}) &= \mathbf{K}. \end{aligned} \quad (106)$$

Annihilation:

$$\begin{aligned}
 T_{1 \rightarrow 2} &= \frac{\pi}{m_a} \frac{n(\mathbf{x}) + 1}{\omega(\mathbf{x})} |(k_1|W|k_2)|^2, \\
 E_{k_1} + \hbar\omega(\mathbf{x}) &= E_{k_2}, \\
 \mathbf{k}_1 + \mathbf{x} - \mathbf{k}_2 &= \mathbf{K}
 \end{aligned}
 \tag{107}$$

We have also written the conditions on the energy and momentum which must be satisfied for the transitions. The scalar function  $W$  is defined by  $W = \mathbf{e}(\mathbf{x}) \cdot \mathbf{W}$ .  $m_a$  in this equation is the mass of the atom, not the electronic mass.

We note here one of the striking features of the momentum conservation rule. A strict conservation of  $\mathbf{k}$  vector is not necessary, but only modulo a reciprocal lattice vector,  $\mathbf{K}$ . It turns out that nonzero vectors  $\mathbf{K}$  are important for the calculation of the resistance of actual metals in all temperature ranges. Scattering processes in which  $K \neq 0$  are called "umklapp" processes in the literature. We also note that for all practical purposes, the electron scattering processes are elastic. The energy of the electrons at the top of the Fermi distribution is high and corresponds to a temperature of the order of  $10^4$  °K, while the maximum phonon energy corresponds to the Debye temperature, and is of the order of  $10^3$  °K for metals. It is thus a very good approximation to ignore the inelasticity of the collisions with the phonons.

### 6.3 Solution of the Boltzmann Equation

With the development of the formulas of (106) and (107) and their interpretation, we are now ready to return to the discussion of the Boltzmann equation, (89), and specifically the term  $(\partial f / \partial t)_{\text{coll}}$ . The rate of change of the number of electrons in state  $\mathbf{k}$ ,  $(\partial f / \partial t)_{\text{coll}}$  is just the rate of transition into the state minus the rate of transition out of the state, integrated over all states to which, or from which, the transition can occur. Thus

$$(\partial f / \partial t)_{\text{coll}} = \int_{\mathbf{k}_1} [T_{2 \rightarrow 1} f_2 (1 - f_1) - T_{1 \rightarrow 2} f_1 (1 - f_2)] d\mathbf{k}_2. \tag{108}$$

In this integration, we have to multiply  $T_{2 \rightarrow 1}$  by  $f_2$  and by  $(1 - f_1)$  because these give respectively the number of particles able to undergo the transition and the probability that the final state is vacant so that the Pauli principle can be satisfied. A contribution to the  $T$ 's of this formula is made both from an annihilation and a creation process, and the  $\mathbf{x}$  vector of the phonon



created is the negative of the  $\kappa$  of the phonon destroyed. Hence, we can simply add the  $T_{2 \rightarrow 1}$  from each of the equations of (107), and we have

$$T_{2 \rightarrow 1} = \frac{\pi}{m_a \omega} |(k_2|W|k_1)|^2 (n(\kappa) + n(-\kappa) + 1). \quad (109)$$

In any crystal which possesses a center of inversion, the energy of a phonon cannot depend on whether it is going in the plus  $\kappa$ -direction or the minus  $\kappa$ -direction, and we make this assumption for our case. Since the number of phonons in a given oscillator at equilibrium is only dependent on the energy,  $n(\kappa) = n(-\kappa)$ . We shall also assume from now on that we are dealing with a temperature well above the Debye temperature of the solid. Hence  $n(\kappa) \gg 1$ , and we can write

$$\left. \frac{\partial f}{\partial t} \right|_{\text{coll}} = \frac{2\pi}{m_a} \int \frac{n(\kappa)}{\omega(\kappa)} |(1|W|2)|^2 \{f_2(1-f_1) - f_1(1-f_2)\}. \quad (110)$$

In (110), we have made use of the Hermitian character of the matrix  $W$ .

We now recall the nature of the problem we are trying to solve. The Boltzmann equation, (89), (110) and (97) is an integro-differential equation for  $f(\mathbf{k})$  which of course is intractable in any but the simplest cases. We shall now assume that the solution in our case is of the form

$$f(\mathbf{k}) = f_0(E) + g(\mathbf{k}). \quad (111)$$

$f_0$  is the Fermi function (i.e., zero field equilibrium) and  $g$  is a small correction of first order in the field  $F$ . Presumably there are other terms in ascending powers of the field, which are negligible. Making this substitution in (110), the first nonzero terms are

$$\left. \frac{\partial f}{\partial t} \right|_{\text{coll}} = \frac{2\pi}{m_a} \int \frac{n(\kappa)}{\omega(\kappa)} |(1|W|2)|^2 [g(\mathbf{k}_2) - g(\mathbf{k}_1)] d\mathbf{k}_2. \quad (112)$$

Since we only integrate over  $\mathbf{k}_2$ ,

$$\left( \frac{\partial f}{\partial t} \right)_{\text{coll}} = -\frac{2\pi}{m_a} g(\mathbf{k}_1) \int \frac{n(\kappa)}{\omega(\kappa)} |(1|W|2)|^2 \left[ 1 - \frac{g(\mathbf{k}_2)}{g(\mathbf{k}_1)} \right] d\mathbf{k}_2. \quad (113)$$

If we write (113) in the form

$$\begin{aligned} \left( \frac{\partial f}{\partial t} \right)_{\text{coll}} &= -\frac{g(\mathbf{k}_1)}{\tau(\mathbf{k}_1)}, \\ \frac{1}{\tau(\mathbf{k}_1)} &= \frac{2\pi}{m_a} \int \frac{n(\kappa)}{\omega(\kappa)} |(1|W|2)|^2 \left[ 1 - \frac{g(\mathbf{k}_2)}{g(\mathbf{k}_1)} \right] d\mathbf{k}_2, \end{aligned} \quad (114)$$

we shall conform to the usual notation, and bring into focus the fact that we are trying to write the scattering process as a relaxation process. We have not quite succeeded yet, however, for as we shall see in a moment we can do this when we are able to eliminate from the expression for  $\tau(\mathbf{k})$  any mention of the unknown function  $g(\mathbf{k})$ . We can proceed by noticing that the Boltzmann equation now reads after (89), (97), (111), and (114)

$$\frac{eF}{\hbar} \frac{\partial f_0}{\partial k_x} = \frac{g(\mathbf{k})}{\tau(\mathbf{k})} \quad (115)$$

In (115), we can make the further reduction  $\partial f_0 / \partial k_x = (\partial f_0 / \partial E) (\partial E / \partial k_x)$ . At this point, we shall make perhaps the most restrictive assumption of all by requiring that  $E(k)$  is given by the effective mass approximation, and moreover that the function  $\tau(\mathbf{k})$  is not a function of direction in the crystal, but only a function of the magnitude of  $\mathbf{k}$ . This assumption amounts to assuming that the energy surfaces of the crystal are spherical and also that the crystal is elastically isotropic, so that  $n(\kappa)$  and  $\omega(\kappa)$  also do not depend on direction in the crystal. Of course, no real crystal fulfills this assumption even approximately, and at this point our discussion takes on a distinctly qualitative flavour. Now, however, we can solve the problem, for (115) becomes

$$\left( \frac{eF}{\hbar} \frac{\hbar^2}{m^*} \frac{\partial f_0}{\partial E} \tau(k) \right) k_x = g(k). \quad (116)$$

Since the quantity in brackets is now only a function of the energy (because of the assumption that  $\tau(k)$  is only a function of the magnitude of  $\mathbf{k}$ ),  $g(\mathbf{k})$  must have the form

$$g(\mathbf{k}) = k_x \chi(E). \quad (117)$$

From (114), and making use of the fact that  $E(k_1) = E(k_2)$ , we now write the relaxation time as

$$\tau(k) = \frac{1}{m_a} \int \frac{n(\kappa)}{\omega(\kappa)} |1|W|2|^2 (1 - \cos \theta) d\mathbf{k}_2. \quad (118)$$

$\theta$  is the angle between  $\mathbf{k}_2$  and  $\mathbf{k}_1$ . In this formula,  $\mathbf{k}_1$  can be assumed to lie in the  $Z$  direction since  $\tau(k_1)$  does not depend upon the direction of  $\mathbf{k}_1$ . We have now indeed solved the problem, and have also written  $\tau(k)$  as a true relaxation time, since (118) does not contain the unknown function  $g(\mathbf{k})$  and presumably can be computed. The Boltzmann equation is integrated now, because (116) together with (118) forms the solution.

The relaxation time solution which we have found has an extremely simple meaning. Suppose that we have displaced the distribution of the

electrons to a nonequilibrium point in phase space, and then let it relax by means of the collision term which we have just calculated. Then we have

$$\frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau}. \quad (119)$$

The solution is simply

$$f - f_0 = (f_{\text{initial}} - f_0)e^{-t/\tau}. \quad (120)$$

The deviation from equilibrium decays in an exponential manner, where  $\tau$  is the decay time.

The reader should not be impressed by our solution of the Boltzmann integro-differential equation. What we have done is to guess a solution in an extremely simplified case, where the essential complexities of the equation are circumvented. Much interesting work has been done to generalize the solutions by trying to determine the most general situation where the equation can be solved by a relaxation time, and by trying to obtain solutions where no relaxation time can be defined. We refer the reader to the review article by Jones and to the original literature for further details.<sup>24</sup>

Another simple result follows from Eq. (115). We can express the solution as

$$f(k) = f_0 \left( k_x, k_y, k_z - \frac{eF}{\hbar} \tau \right). \quad (121)$$

That is to say, the whole equilibrium Fermi distribution has simply been displaced under the action of the electric field and the collision relaxation by an amount along the  $k_x$  direction of  $eF\tau/\hbar$ . This is the solution we have already alluded to in an earlier part of this section. We can obtain from (121) an expression for the total current, and thus also for the conductivity. Since we have simply moved the centre of gravity of the distribution by the amount  $eF\tau/\hbar$ , we have a total current of

$$j_x = \frac{e^2 FN \tau}{m^*} \quad (122)$$

(momentum divided by mass and multiplied by  $e$ ). The conductivity is

$$\sigma = \frac{e^2 \tau N}{m^*} \quad (123)$$

This result is the same as the classical result derived by Drude and Lorentz, but the meaning of the effective mass and the relaxation time must be taken from the quantum theory of the solid.

### 6.4 Calculation of the Relaxation Time

In principle, we have solved the conductivity problem for our simplified model of a metal in the previous paragraphs. However, the integral for the relaxation time was left in a general form. The computation of this integral is by no means a simple operation in practice, even when the restrictive assumptions which we made in order to derive it are imposed. Two general types of difficulty arise. One difficulty has to do with counting all the ways the electrons can be scattered by the phonons. It will be remembered that the scattering was supposed to be elastic, but could be partly "umklapp," in which the electron is essentially scattered from one  $B$ -zone into another. An accurate counting method would involve a knowledge of the function  $\omega(\kappa)$  for the phonons and the density of states function for the electrons. Usually, both of these quantities are only approximately known for a solid. The second general difficulty comes up in the computation of the scattering Hamiltonian and the scattering matrix. We shall have opportunity for only a very simplified treatment here, and the reader is referred to the Jones article<sup>24</sup> for an excellent review of the techniques which have been developed for reduction of the problem

The relaxation time is given by

$$\frac{1}{\tau(\vec{k})} = \frac{2\pi}{m_a} \left( \frac{L}{2\pi} \right)^3 \int d\mathbf{k}_1 \frac{n(\kappa)}{\omega(\kappa)} |(1|W|2)|^2 (1 - \cos \theta) \delta(E_{k_1} - E_k). \quad (124)$$

We shall restrict ourselves to the high temperature case in which the number of phonons present in any oscillator is given by the classical limit. When  $kT \gg \hbar\omega$ , we can represent the Bose-Einstein distribution (86), by the equipartition law,

$$n = \frac{kT}{\hbar\omega} \quad (125)$$

For clarity, Boltzmann's constant is written  $k$ , the wave vector as  $\vec{k}$ . It will be necessary to make some assumption for the form of  $\omega(\kappa)$ , and we shall assume that it is given by the Debye approximation,

$$\omega = c\kappa, \quad (126)$$

in which the velocity of sound,  $c$ , is a constant and not dependent on frequency. If we used the formula (126) as it stands, the velocity of sound would be a characteristic parameter of the solid, and it is usual to represent this parameter as the Debye temperature instead, which we have introduced in (88). Putting (88) and (87) together, we can write (126) as

$$\omega(\kappa) = \kappa \frac{L}{N^{1/3}} \left( \frac{1}{6\pi^2} \right)^{1/3} \frac{k\theta}{\hbar} \quad (127)$$

Finally, we note that the integration over  $d\mathbf{k}_2$  in the relaxation time, (124), is to be taken over a delta function in the energy. If we write the volume element as  $d\mathbf{k}_2 = k^2 dk d(\cos \theta) d\varphi$  and then as  $(m^*/\hbar^2)k dE d(\cos \theta) d\varphi$ , the integration becomes

$$\frac{1}{\tau(\hbar)} = (6\pi^2)^{2/3} \frac{m^*}{m_a} \frac{kNa}{h} \frac{T}{k\theta^2} \int_{-1}^{+1} d(\cos \theta) \frac{|(1|W|2)|^2}{x^2} (1 - \cos \theta). \quad (128)$$

In this formula, we have defined the quantity  $a$ , which is related to the lattice parameter, by the relation  $L^3/N = a^3$ .

According to (123), the resistivity of the metal is proportional to the relaxation time, and hence the resistivity of a sample at high temperatures is proportional to the first power of the temperature. This proportionality is observed. In fact, the resistivity for Na based on the foregoing formulas leads to very good agreement with the experimental value.<sup>24</sup> In view of the extensive approximations we have had to make in the argument, this agreement must be regarded as fortuitous and is not to be taken as reason for a wide and uncritical applicability of the formulas.

There is one further point which we can make at the close of this discussion. We can now verify a comment made earlier that the solid at zero degrees does not scatter its electrons, and the electron functions can thus be written as Bloch waves. The reason is simply that energy must be conserved, and the Pauli principle must remain satisfied. Hence if we try to scatter an electron on the Fermi surface, we have no states to scatter it into. (In this statement, we specifically exclude the superconductors.) On the other hand, if we introduce an excited electron into the solid at zero degrees, phonons will be created in the various oscillators and scattering will take place until the energy of the electron has been turned into heat energy of the solid as a whole.

## 7. Imperfections

The largest part of our discussion of the quantum theory of solids has to do with the perfect solid. That is, the lattice, apart from the vibrations of the atoms, has been assumed to be a perfectly regular structure. The real solid differs from this model in two important ways. It will have various types of imperfections in the lattice structure, and it will possess discrepancies in the chemical composition. For example, a bar of copper will have a certain fraction of its atoms displaced from their normal positions in the lattice, and there will be a certain amount of impurity always present in the form of other kinds of atoms. For many properties of the solid, we can

neglect these imperfections. For example, if the imperfections content is small, of the order of a fraction of a percent, the measured cohesive energy, or specific heat, etc., will be that calculated for a perfect crystal. On the other hand, the conductivity of a metal at low temperatures is very high because of the noninterference with the free flight of an electron through the perfect metal, and the presence of a very minute amount of imperfection in the crystal is sufficient to alter the picture in a fundamental way. Hence, there is a class of properties of the solid, called the structure sensitive properties, where a theory must include the effects of the imperfections.

We shall conclude this chapter with a discussion of how the band structure of a solid is changed with the addition of imperfections. For a very excellent semiquantitative treatment of imperfection problems, the reader is referred to the article by Seitz in "Imperfections in Nearly Perfect Crystals."<sup>25</sup> Seitz has made the following list of general types of primary imperfections: phonons, electrons and holes, excitons, vacant lattice sites, and interstitial atoms, foreign atoms in either interstitial or substitutional positions, and dislocations. Seitz' viewpoint is that the perfectly periodic solid at absolute zero is the perfect solid, and hence phonons and electrons are included, because in insulators neither of these particles is present at absolute zero. We have, of course, already discussed these "imperfections," and it is the rest of the list which will take our attention now.

An exciton is best described as being an electron and a hole in an insulator coupled together in hydrogen atom fashion by their coulomb fields. The classic example is the NaCl crystal. This crystal is transparent to visible light because the band gap is large enough that the energy of the photon is insufficient to excite an electron from the filled to the next unfilled band. However, as the photon energy is increased, a series of peaks is observed in the absorption spectrum of the crystal just before the "fundamental" absorption is reached. The fundamental absorption corresponds to the excitation of free electrons into the unfilled band and free holes into the filled band. The peaks, however, are associated with the creation of electrons and holes which are bound to each other in hydrogenlike orbits. The binding energy is small, of the order of a few tenths of an electron volt because the dielectric nature of the crystal cuts down the effectiveness of the Coulomb field between the electron and hole. Of course, the exciton is metastable, and the electron and hole eventually annihilate each other and give up their energy to the phonons, but even their transitory existence is important for the absorption curve. They are also thought to be responsible for the production of lattice vacancies, since the energy released when an exciton decays is considerable.

In a vacant lattice site, we extract an atom from the perfect crystal and place it on the surface. Conversely, in the interstitial case, we jam a surface atom into a nonlattice position in a region where all the lattice sites are occupied. Vacancies and interstitials again are important for the ionic crystals, since they represent an effective extra charge in the crystal, and diffusion of the defects corresponds to charge transport in the crystal. It is this charge transport which is responsible for the measurable electrical conductivity of these crystals at elevated temperatures. On the other hand, in a metal or semiconductor, these same defects contribute to the electrical resistivity, since electrons are very efficiently scattered by them. In fact, the low temperature conductivity of a normal metal never goes to infinity as predicted by our formulas of the last section because of the presence of finite numbers of impurities, vacancies and interstitials. In fact, one of the ways of studying the amount of damage done to a crystal by energetic protons, deuterons, neutrons, etc., is to measure the increase in the "residual" resistivity at low temperatures

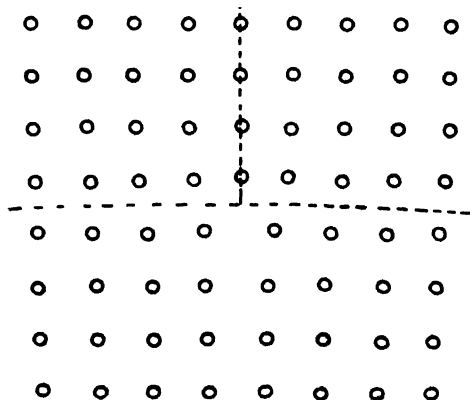


FIG. 10. An edge type dislocation in a cubic lattice. Note that the dislocation is constructed by forcing an extra plane of atoms (perpendicular to the page) into part of the crystal. Around the region where the plane ends, there is considerable distortion of the lattice. The defect can "move" from one region to another by shifting the atoms slightly from the positions of the figure until another row of atoms becomes the extra plane.

One of the most important experimental developments of recent years in the field of solids is the gradual perfection of techniques for controlling the impurity content of solids. It is now quite easy to bring the impurity content of a germanium sample down to one part in  $10^8$ . The practical

importance in this case is due to the fact that impurities contribute free electron or hole current carriers at room temperature. The mechanical properties of crystals also are markedly affected by small amounts of impurities. As we shall mention in the next paragraph, the plastic flow of a crystal is due to the presence of a defect called a dislocation. If there is a marked tendency for the impurities to segregate near the dislocations, which is sometimes the case, the motion of the dislocations will be impeded.

A dislocation in a crystal is the lattice imperfection which allows the crystal to "flow" under sufficient stress. One can calculate the stress necessary to move the atoms over one another in a perfect crystal for a given force law between the atoms. On the other hand, an actual crystal will begin to be plastic well before this theoretical stress is reached. The reason is the dislocation, which will move at the lower stress level. One can see from Fig. 10 how, as the dislocation moves from left to right, the top part of the crystal becomes sheared by one lattice spacing with respect to the bottom. We have pictured a so-called edge type dislocation in the figure. There are other types than this one, but we refer the reader to the literature for further discussion of this highly interesting defect.

### 7.1 Band Structure in a Defect Crystal

As the final section of this chapter, we shall show what changes one must make in the foregoing discussion of the band structure of the perfect crystal when there are imperfections present. Slater has given a particularly beautiful treatment of the subject,<sup>26</sup> and the reader is referred to his article for more details than we can bring into our discussion.

For the sake of definiteness, let us suppose that we have an impurity atom in our crystal which may be looked on as a local variation in the otherwise periodic potential. We will write the total Hamiltonian as

$$H = H_0 + H'. \quad (129)$$

$H_0$  is the perfect crystal Hamiltonian which yields the set of Bloch wave functions,  $\psi_{\mathbf{k}}(\mathbf{x})$ , and the energy,  $E(\mathbf{k})$ .  $H'$  is the local variation in this potential due to the defect. In the solution of the problem, it will be important to introduce a new set of orthogonal functions, called the Wannier functions, which are constructed from the Bloch functions, but which are localized functions. Each Wannier function belongs to a particular lattice site,  $\mathbf{R}_j$ . These functions are thus analogous to the  $\chi(\mathbf{x} - \mathbf{R}_j)$  functions of the Bloch tight binding method, except that the Wannier functions for



different lattice sites are rigorously orthogonal to each other. The Wannier functions are defined by

$$a(\mathbf{x} - \mathbf{R}_l) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k} \cdot \mathbf{R}_l} \psi_{\mathbf{k}}(\mathbf{x}). \quad (130)$$

We can see immediately that these functions are highly peaked in the corresponding cell,  $\mathbf{R}_l$ , by writing the function for the free electron case, where the Bloch function is a running wave. Then the Wannier function for the cell at the origin of a one dimensional crystal is proportional to  $\sin(2\pi N x/L)/\sin(2\pi x/L)$ . The functions are orthogonal because of the orthogonality of the Bloch functions for different  $\mathbf{k}$ , and the completeness theorem, (65)

$$\begin{aligned} \int a^*(\mathbf{x} - \mathbf{R}_l) a(\mathbf{x} - \mathbf{R}_l) d\mathbf{x} &= \frac{1}{N} \sum_{\mathbf{k}, \mathbf{k}'} e^{i(\mathbf{k}' \cdot \mathbf{R}_l - \mathbf{k} \cdot \mathbf{R}_l)} \int \psi_{\mathbf{k}'}^* \psi_{\mathbf{k}} d\mathbf{x} \\ &= \frac{1}{N} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{R}_l - \mathbf{R}_l)} = \delta_{\mathbf{R}_l, \mathbf{R}_l + \mathbf{K}}. \end{aligned} \quad (131)$$

The Wannier functions can now be used as a set of basis functions for the solution of the total Hamiltonian in the Schrödinger equation. That is, let us assume that the solution may be written as

$$\begin{aligned} H\Psi &= E\Psi \\ \Psi &= \sum U(\mathbf{R}_l) a(\mathbf{x} - \mathbf{R}_l) \end{aligned} \quad (132)$$

The  $U$ 's are the expansion coefficients. If we substitute the second equation into the first, multiply on the left by  $a^*(\mathbf{x} - \mathbf{R}_l)$  and integrate, we have

$$\begin{aligned} \sum_{\mathbf{R}_l} U(\mathbf{R}_l) \int a^*(\mathbf{x} - \mathbf{R}_l) H a(\mathbf{x} - \mathbf{R}_l) d\mathbf{x} \\ = E \sum_{\mathbf{R}_l} U(\mathbf{R}_l) \int a^*(\mathbf{x} - \mathbf{R}_l) a(\mathbf{x} - \mathbf{R}_l) d\mathbf{x} = E U(\mathbf{R}_l). \end{aligned} \quad (133)$$

The matrix element for  $H_0$  is written

$$a^*(\mathbf{x} - \mathbf{R}_l) H_0 a(\mathbf{x} - \mathbf{R}_l) d\mathbf{x} = \frac{1}{N} \sum E(\mathbf{k}) e^{i\mathbf{k} \cdot (\mathbf{R}_l - \mathbf{R}_l)} = \varepsilon(\mathbf{R}_l - \mathbf{R}_l). \quad (134)$$

We can also write the inverse Fourier series for  $E(\mathbf{k})$  as

$$E(\mathbf{k}) = \sum_{\mathbf{R}_l} \varepsilon(\mathbf{R}_l) e^{-i\mathbf{k} \cdot \mathbf{R}_l}. \quad (135)$$

Finally, we have transformed the Schrödinger equation for  $\Psi$  into a difference equation for the expansion coefficients,  $U(\mathbf{R}_j)$ ,

$$\sum_{\mathbf{R}_j} \{\varepsilon(\mathbf{R}_i - \mathbf{R}_j) + H'(\mathbf{R}_i, \mathbf{R}_j)\} U(\mathbf{R}_j) = EU(\mathbf{R}_i) \quad (136)$$

$$H'(\mathbf{R}_i, \mathbf{R}_j) = \int a^*(\mathbf{x} - \mathbf{R}_i) H' a(\mathbf{x} - \mathbf{R}_j) d\mathbf{x}.$$

The solution of this difference equation is the solution of the problem of the defect in the crystal. The difference equation is of course difficult to solve in the general case, but we can make some approximations which make it tractable. For instance, consider the case where the  $H'$  function is slowly varying over a cell. Then, since the Wannier functions are orthogonal to one another, and are more or less localized in the space of a single cell, the matrix for  $H'(\mathbf{R}_i, \mathbf{R}_j)$  is nearly zero when  $\mathbf{R}_i$  is unequal to  $\mathbf{R}_j$ . We shall thus neglect all the nondiagonal elements of  $H'$ .

In (136) we have terms in  $\varepsilon$ , which we shall write

$$\sum_{\mathbf{R}_j} \varepsilon(\mathbf{R}_i - \mathbf{R}_j) U(\mathbf{R}_j) = \sum_{\mathbf{R}_s} \varepsilon(\mathbf{R}_s) U(\mathbf{R}_i - \mathbf{R}_s). \quad (137)$$

The function,  $U$ , is defined only for the lattice points as we have written it in (132), but we would like to transform the difference equation into a differential equation. Therefore, let us make  $U$  into a continuous function of its argument, so that it takes on the values at the lattice points which are the solutions to the Eq. (136). Then we can write  $U$  as a Taylor's expansion in the form

$$\begin{aligned} U(\mathbf{R}_i - \mathbf{R}_s) &= U(\mathbf{R}_i) - \mathbf{R}_s \cdot \frac{\partial U(\mathbf{R}_i)}{\partial \mathbf{R}_i} + \dots \\ &= \{e^{-\mathbf{R}_s \cdot \nabla}\} U(\mathbf{R}_i). \end{aligned} \quad (138)$$

(137) now takes the form

$$\sum_{\mathbf{R}_s} \varepsilon(\mathbf{R}_s) U(\mathbf{R}_i - \mathbf{R}_s) = \left\{ \sum_{\mathbf{R}_s} \varepsilon(\mathbf{R}_s) \exp \left[ -i\mathbf{R}_s \cdot \left( \frac{1}{i} \nabla \right) \right] \right\} U(\mathbf{R}_i). \quad (139)$$

The gradient operator in this equation is the gradient with respect to  $\mathbf{R}_i$ . We notice that the operator in the braces is related to the function  $E(\mathbf{k})$ ,

which we have written in (135). The only change is that we have substituted the operator  $(1/i)\nabla$  for the vector  $\mathbf{k}$ . Of course, this is a familiar substitution, because it is the same as setting  $\mathbf{k} = \mathbf{p}/\hbar = (1/i)\nabla$ . We can now write the difference equation as the differential equation

$$\left[ E\left(\frac{1}{i}\nabla\right) + H' \right] U(\mathbf{x}) = EU(\mathbf{x}). \quad (139)$$

The operator  $E(\mathbf{k})$  is the energy obtained from the solution for the perfect crystal with the Hamiltonian,  $H_0$ . We make an operator out of it by substituting  $(1/i)\nabla$  for  $\mathbf{k}$ . The eigenvalue  $E$  on the right is the total energy of the localized electron. In the effective mass approximation,  $E(\mathbf{k})$  can be written as

$$E(\mathbf{k}) = E_0 + \frac{\hbar^2}{2m^*} k^2 + \dots \quad (140)$$

$E_0$  is the bottom of the band.

Equation (139) is frequently called the effective mass equation for a localized defect, because the kinetic energy operator involves the electrons as if particles with an effective mass. We note that the justification for the validity of the effective mass equation is that the local potential  $H'$  is a slowly varying function. If it is not, one must use other terms in the difference equation, and the corresponding equation to (139) is a quite complicated nonlocal equation which is not an ordinary differential equation. Physically, the meaning of (139) is quite clear. If the electron is able to sample a region of the crystal which contains a large number of atoms, and the potential in this region is essentially periodic, then we can define an effective mass for the electrons in the region. Then the energy of an electron will vary continuously from one region to another over the local perturbation.

Let us suppose that the local potential is that of an impurity atom, which has an extra positive charge. Then the local potential,  $H'$ , is nearly Coulombic, and Eq. (139) takes on the appearance of a hydrogen atom Schrödinger equation with discrete localized levels appearing below the band. Exactly this situation occurs in the semiconductor crystals like Si and Ge, and to some extent in the ionic crystals. These crystals have high dielectric constants, so the potential is reasonably slowly varying, and localized levels are created for either holes or electrons in the forbidden energy gaps when impurities are added.



## 7. The Quantum Mechanics of Liquids

H. N. V. Temperley

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There have been three main approaches to the problem of describing the liquid state in quantum mechanical terms. It has been found empirically that various very simple physical models of a classical liquid can each describe some of its properties with considerable success. It is therefore reasonable to try to adapt such models to take account of quantum effects. This can very often be done satisfactorily in the formal sense, but comparison with experiment usually gives only rough agreement — comparable with what can be obtained from purely empirical equations of state with two or three adjustable parameters. A second approach, due to Landau,<sup>1</sup> was based upon the idea that, since the equations of classical hydrodynamics give a satisfactory account of many of the mechanical properties of the liquid, it ought to be possible to generalize them to cases where quantum effects cannot be neglected, by introducing the idea that quantities like the density  $\rho$  and velocity of flow  $v$  are noncommuting quantities, in other words, one looks for some generalization of Heisenberg's uncertainty principle that

might be applicable to a continuous medium rather than to single particles. This approach has been mainly used for liquid helium.

A third approach, based on starting with the actual many-body wave equation and trying to find approximate solutions of it has also had some success. Since the interactions between molecules in a liquid are always very strong, we cannot use any ordinary type of perturbation theory, but we have to think of some special artifices.

We shall be concerned almost entirely with the inert gases, which can safely be regarded as having spherical molecules, and it is also a good approximation to treat their interactions as central, so that the force between two molecules acts along the line joining their centres and depends merely on their distance apart. Also, we shall neglect nonadditivity, i.e., we shall suppose that the interaction between two molecules is unaffected by the proximity of a third. These assumptions certainly prevent us from discussing "associated" liquids like water and the alcohols, for which hydrogen bonds and dipole-dipole interactions can be important, but they do not restrict us entirely to the inert gases. The approximation of regarding other types of molecule as spheres may seem poor, but there are instances of very symmetrical molecules like carbon tetrachloride, to which one can assign a "sphere of influence," since they are probably *rotating* in the liquid state, and a similar approximation can also be made for diatomic molecules and even for "flat" molecules like benzene.

There is probably no liquid for which quantum effects can be completely neglected, but, by going from light to heavy molecules we can progress from helium, in which it is clear that quantum effects are of major importance, through the inert gases and other symmetrical molecules, to cases where the quantum effects become of minor importance. It is possible to set up a rough criterion which enables us to decide their probable importance. Consider a molecule of liquid. It can be thought of, roughly, as having access to a volume of the order of  $V/N$ , where  $V$  is the total volume and  $N$  the number of molecules. That is, the energy levels of a particle moving about in a "box" of linear dimension  $d$  ( $d^3 \approx V/N$ ) will have a separation comparable with  $h^2/md^2$ . If this quantity is small compared with  $kT$ , where  $k$  is Boltzmann's constant, then we can regard the distribution of energy levels as practically continuous, and a classical treatment would be reasonable. If it is comparable with  $kT$ , quantum effects would be very important. We can easily see that the latter will be the case for helium, for we have  $d \sim 3.5 \times 10^{-8}$  cm,  $T \sim 4^\circ$  K so that the ratio

$$\frac{h^2}{md^2kT} \approx 10. \quad (1)$$

As we increase our molecular weight, the temperature,  $T$ , corresponding to the liquid region, also rises slowly, but the order of magnitude of  $d$  does not change since nearly all nonmetallic liquids have a density of the order 1 to 2 gm/cm<sup>3</sup>. We know, because of the small value of  $m$ , that the electrons in liquid metals have to be treated quantum mechanically even if the positive ions do not. It is, in fact, quite difficult to find a case in which the parameter (1) is completely negligible compared with unity, though we should not expect other liquids to show the extreme "quantum-like" behaviour of helium, and, in fact, they do not. Except for a few other cases, such as hydrogen and neon, a purely classical treatment is a decent first approximation, but, as with solids, it is difficult to find any region of temperature in which quantum effects are wholly negligible.

### 1. de Boer's Extension of the Principle of Corresponding States

If we have purely classical conditions, some of the difficulties of computing the thermodynamic properties of a liquid disappear. In particular, a law of corresponding states is found, empirically, to be a reasonably valid approximation for "simple" (nonassociated) liquids, and their vapours. We recall that a van der Waals' or similar type of equation of state, containing not more than two empirical constants, takes the same form for all substances if the pressure, volume and temperature are expressed as multiples of their values at the critical point. In other words, if we write  $P^* = P/P_c$ ,  $T^* = T/T_c$ ,  $V^* = V/V_c$ , the law asserts that the relation between  $P^*$ ,  $V^*$ , and  $T^*$  should be the same for all substances. So far, the argument is that a considerable range of data on liquids and vapours can be *empirically* represented by means of fairly simple equations, and the law of corresponding states then follows as a first approximation if these equations do not contain too many arbitrary constants. The correlation between the properties of a series of *similar* substances, such as chemically similar compounds or homologous series, is sometimes quite remarkably good. The law was originally interpreted in terms of empirical equations of state, but it can be given a much sounder basis without resorting to any actual model of the liquid state, and the new treatment also shows us in what way "quantum complications" enter into such a problem. We assume that the forces between two molecules (assumed central and additive as before) can be represented by means of a universal function, thus

$$V(r_{12}) = \epsilon f(r_{12}/\sigma) \quad (2)$$

where  $f$  is the same for all substances and  $\epsilon$  and  $\sigma$  are scaling constants characteristic of each substance. We shall show that such an assumption

has a law of corresponding states as a rigorous consequence in the classical limit. The proof is quite independent of the actual form of  $f$ , but, in practice, it will involve repulsion between the molecules at short separations and attraction at large separations. This assumption is by no means as restrictive as at first sight appears, indeed, it is probably a satisfactory approximation in all cases for which the forces can be considered to be central at all. The "Lennard-Jones" type of interaction, in which the attractive and repulsive parts of the interaction are both represented by power laws, can always be put into the above form. If the electron distribution round the molecule is reasonably symmetrical, then it is to be expected that the attraction will be of inverse sixth power type, the so-called "London-van der Waals interaction". The repulsion is usually represented by a high inverse power (12 or 14) and work on the second virial coefficient of gases shows that this cannot be too far from the truth, and also that it makes very little difference what power one actually uses for this repulsive term.

Thus, we conclude that assumption (2) is a good approximation for simple molecules. The parameters  $\epsilon$  and  $\sigma$  are at our disposal,  $\epsilon$  measuring the *intensity* of the forces, being proportional, for example, to the minimum in the energy curve, while  $\sigma$  is a measure of the *range* of the forces, thus resembling the "gas-kinetic diameter." Some standard results of statistical mechanics now enable us to write down the "Slater sum over states," and thence to determine all the equilibrium properties. This sum, which generalizes the concept of "partition function," can be written, for a vessel with a fixed number of molecules,

$$Z = \int \sum_{(n)} (\psi_k^* \exp [-(\mathcal{F} + \mathcal{V})/kT] \psi_k) dv_n \quad (3)$$

where the summation is over a complete set of states appropriate to  $N$  molecules inside the volume of the vessel,  $\mathcal{F}$  and  $\mathcal{V}$  representing the kinetic and potential energy operators making up the Hamiltonian. The  $N$  integrations are one for each particle, the volume of the vessel being the domain of integration. The expression for  $Z$ , being a diagonal sum, is independent of the choice of wave functions. If we knew the eigenfunctions of the problem, they could be inserted into (3), and expanding the exponential and using the relationship  $(\mathcal{F} + \mathcal{V})^n \psi_k = E_k^n \psi_k$  we find that  $Z$  is equivalent to  $\sum \exp(-E_k/kT)$ , (degenerate levels being reckoned the appropriate number of times in such sums).

We now examine what happens if we neglect the noncommutation of  $\mathcal{F}$  and  $\mathcal{V}$ , so that we may write

$$\exp [-(\mathcal{F} + \mathcal{V})/kT] \approx \exp(-\mathcal{V}/kT) \exp(-\mathcal{F}/kT). \quad (4)$$



This is always true as a first approximation but in fact, there are, always terms involving the various commutators like  $\mathcal{T}\mathcal{V} - \mathcal{V}\mathcal{T}$  which ought to be considered. In the classical limit we neglect these, and it also turns out to be permissible to neglect symmetry properties of our wave functions. Since any complete set may be inserted into (3) we choose those appropriate to free particles. For simplicity, suppose that our vessel is a cube of side  $d$ , the appropriate wave functions vanishing at the walls, are, for just one molecule,

$$\psi = \sin\left(\frac{p\pi x_n}{d}\right) \sin\left(\frac{q\pi y_n}{d}\right) \sin\left(\frac{r\pi z_n}{d}\right) \quad (5)$$

(Vol. I, Chapter 3, § 1),  $p$ ,  $q$  and  $r$  being positive integers. Under "classical" conditions, we can neglect symmetry properties and the appropriate wave functions for a set of  $N$  molecules will simply be a product of  $N$  functions of the type (5). The form of the operator  $\mathcal{T}$  is quite unaffected by the form of  $\mathcal{V}$  and may be written

$$\mathcal{T} = \frac{\hbar^2}{8\pi^2m} \sum_n \nabla_n^2$$

each of which operators in the sum will affect only the wave function with corresponding coordinates. Thus, to this approximation, each of the separate kinetic energy operators introduces into (3) a factor

$$\exp\left[\frac{-\hbar^2}{8d^2mkT}(p^2 + q^2 + r^2)\right].$$

There will be one such factor for each molecule, and  $p$ ,  $q$ , and  $r$  can take all positive integral values for each one, so that the operation  $S$  now implies summation over all these values for each molecule in term. For nearly all purposes, the summations over  $p$ ,  $q$ ,  $r$  can be replaced by an integration, and we have, since

$$\begin{aligned} \int_0^\infty \exp(-ax^2) dx &= \sqrt{\pi/4a}, \\ \sum_{p=1}^\infty \exp\left(\frac{-\hbar^2 p^2}{8d^2mkT}\right) &\sim \frac{(2\pi mkT)^{1/2}d}{h} \end{aligned} \quad (6)$$

so that the effect of the kinetic energy may be represented, in the classical approximation, as simply contributing to  $Z$  a factor that is the  $3N$ th power of expression (6), i.e., a factor  $(\text{const.} \times T^{3/2} \times V)^N$ . If there is no potential energy, the resulting  $Z$  can be handled by statistical thermodynamics, and

the standard procedures would give us simply the equation of state of a perfect gas.

The remaining problem is to estimate the effect of the potential energy in (3), and it must be said at once that it has not yet been solved for dense gases or liquids for any realistic form of interaction energy. We can, nevertheless, deduce the law of corresponding states as a consequence of assumptions (2) and (4). For, if we remove from  $Z$  the factors corresponding to the kinetic energy  $\mathcal{T}$ , expression (3) now calls simply for an averaging of  $\exp(-\mathcal{V}/kT)$ , where we are free to use any convenient set of wave functions. If we use again the free-particle wave functions, (3) simply calls for an averaging over all possible positions of all the molecules of the Boltzmann factor corresponding to the total potential energy. We have thus arrived at a result equivalent to a treatment based entirely on classical ideas, according to which we average the Boltzmann factor over all velocities and all positions of all the molecules. If, for  $\mathcal{V}$ , we insert a sum of expressions like (2) over all pairs of molecules, we conclude that

$$V^N \int_{(N)} S \psi_k^* \exp(-\mathcal{V}/kT) \psi_k dv_n = \int_{(N)} \exp\left(-\sum V_{ij}/kT\right) dx, dy, dz, \quad (7)$$

and using (2) it then follows that

$$Z = T^{3N/2} f(T/\varepsilon, V/\sigma^3) \quad (8)$$

since  $\varepsilon$  can only enter (7) through the ratio  $T/\varepsilon$ , and variations of  $\sigma$  can be taken care of completely by a change of scale of the coordinates in the integration over the volume of the vessel.

The standard formulas of thermodynamics now give

$$S = \frac{\partial}{\partial T} (kT \log Z), \quad P = \frac{\partial}{\partial V} (kT \log Z)$$

from which it is evident that  $P \sigma^3/\varepsilon$  should depend only on  $kT/\varepsilon$  and  $V/N\sigma^3$  which is the law of corresponding states. It should be noticed particularly that there is no such law for internal energy or specific heat, because of the kinetic factor  $T^{3N/2}$  in  $Z$  which leads to a contribution  $\frac{3}{2}kT$  to the energy. It is possible for the molecule to have *internal* degrees of freedom, (e.g., different separations of the two atoms in a diatomic molecule) without the interaction energy being greatly affected. In such a case, we should have further terms in the energy and specific heat, but still a law of corresponding states for the pressure. In the above treatment, we have tacitly assumed that our molecules are effectively monatomic, but there is no difficulty in allowing for internal degrees of freedom, since a change in the

rotational or vibrational state of a molecule does not greatly affect its interaction with others.

It is now easy to see how the failure of assumption (4) will lead to a departure from the law of corresponding states, and to determine what the form of this departure must be. To allow for the lack of commutation of  $\mathcal{T}$  and  $\mathcal{V}$ , it would be necessary to introduce into (4) a further factor involving the exponential of  $(\mathcal{T}\mathcal{V} - \mathcal{V}\mathcal{T})/k^2T^2$  to a first approximation, and further corrections involving commutators of higher order may also be required. Since this implies two differentiations with respect to the coordinates, we see, using (2) that our correction must be a factor involving the quantity  $\hbar^2\epsilon/m\sigma^2T^2$  so that there is now another possible variable on which  $P\sigma^3/\epsilon$  can depend, besides  $kT/\epsilon$  and  $V/N\sigma^3$ . (The extra variable introduced by de Boer is  $\Lambda^* = \hbar/(m\epsilon)^{1/2}\sigma$ .) It is easy to verify that no further variable is introduced by the higher commutators, (which merely imply that the correct sum over states has to be expressed in ascending powers of  $\hbar^2$ ). de Boer's parameter has a simple physical meaning,  $\epsilon$  is a measure of the typical energy of one molecule, and  $\hbar/(m\epsilon)^{1/2}$  is proportional to the de Broglie wavelength associated with that energy, while  $\sigma$  is a measure of the effective size of the molecule. If the de Broglie wavelength is not small compared with molecular dimensions, we may expect a "quantum departure" from the law of corresponding states, and this departure should vary with  $\Lambda^*$ .

A remarkable application of this simple idea was made by de Boer.<sup>2</sup> By comparing data from light atoms and molecules he was able to predict the approximate temperature and density of liquefaction of  $\text{He}_3$ , at a time when it had not been liquefied, and there was some doubt whether it would liquefy at all. Since  $\text{He}_4$ ,  $\text{H}_2$ , and  $\text{D}_2$  molecules all are described by symmetrical wave functions, while  $\text{He}_3$  must be described by antisymmetrical wave functions, the quantitative success of these predictions is rather surprising. It suggests that, in the "near-classical" region of small  $\Lambda^*$ , the effect of noncommutation of kinetic and potential energies is more important than that of symmetry. When we come to the liquids themselves, the departure from classical conditions is very great, and the great difference between the properties of the two He liquids is clear evidence of the importance of symmetry effects in the actual liquid region.

## 2. Some Simple Liquid Models

We proceed to describe a few of the concepts that have proved helpful in discussing liquids. In some cases, purely classical ideas are involved, though we are free to try to graft on "quantum corrections" if we want to,

in others quantum effects are fundamental from the start. The present position is confusing, in that it is possible to describe very many of the properties of a liquid if we are allowed to select the model most suited to each set of properties, but we cannot, yet, compare their predictions with experiment and "decide" between alternative possibilities. The truth seems to be that, while the various models are, in some respects, inconsistent, yet any two of them probably have some common region of validity and the present function of experiment is probably to determine this. Most of the models will only be described very briefly.

## 2.1 Models Based on Purely Classical Concepts

Possibly the simplest is the "cell" model. According to this, we fix our attention on a typical molecule, which is supposed to be moving about in a potential field representing the "smoothed" effect of the remaining molecules. Various degrees of refinement are possible, for example we may simply think of our molecule in a steep-sided potential well, with the potential practically constant inside, or we may suppose the potential to increase parabolically with distance from the centre of the cell, so that the motion of our molecule resembles that of a simple harmonic oscillator. We can choose the constants of the cell by direct reference to experiment, or we can attempt, as in the work of Lennard-Jones and Devonshire, to calculate the "cell field," in terms of a known intermolecular interaction, by averaging over various possible configurations of the neighbouring molecules. Actually, it is rather interesting that such calculations show that the parabolic approximation to the potential is good at high densities, but that a practically constant potential inside the cell is more realistic at low densities. Any attempt to "decide between" these two possibilities experimentally could, therefore, have led to no definite conclusion and this is the sort of situation that constantly confronts us in this field.

An apparently quite different model is based on the concept of "holes". Again, this can take various forms. We may think of a hole simply as a vapour bubble in the liquid, its motion through the liquid and its expansion and contraction resulting in the pushing aside of other molecules. The kinetic energy associated with such motion can, if we wish, be ascribed to "virtual masses" as in hydrodynamics, while the "potential energy" of the hole is simply the energy required to create the surface against the intermolecular forces. Another variant of this concept is that the hole is thought of as a vacancy in an otherwise fairly perfect crystal lattice, a liquid thus

being thought of as like a solid that has lost its perfectly ordered structure, as a result of a percentage of the molecules occupying interstitial sites and leaving vacancies at some of the real lattice sites. It is even possible to think of a liquid as being equivalent, for statistical mechanical purposes, to a sort of equilibrium mixture of fragments of crystal lattice ranging in size from a few molecules upwards.

Over the years, emphasis has gradually shifted towards treating a liquid as a solid which has lost its long range structure, in preference to the older conception of an imperfect gas where interactions have proved strong enough to lead to a transition. Here again, a "decision" between these two concepts is impossible and inappropriate, probably because the former concept is useful near freezing point, where the liquid density differs little from that of a solid, while the latter concept is valuable in the critical region. There is, however, one further concept that does enable us to combine these two ideas to a considerable extent, namely that the quantity most suited to describe the liquid state is the *distribution function*,<sup>3</sup> which replaces the mean molecular distance in a gas and the lattice structure in a solid. We define the distribution function as a function of the polar variable  $r$ . A typical liquid molecule is taken as the origin, and  $g(r)$  is defined as proportional to the probability of finding another molecule in any small volume at a distance  $r$  from the origin. The general behaviour of this function is known from geometrical considerations and simple common sense. In a solid, we may think of each molecule as surrounded by "Chinese boxes" made up of sets of other molecules at various distances, each molecule being surrounded first by its nearest neighbours, then by its second nearest neighbours and so on. At large distances, this function varies with the periodicity of the lattice, in a way that depends on the inclination of the radius vector  $r$  to the crystal axes.

The behaviour of the distribution function in a liquid is a sort of "smeared" version of that in a crystal lattice. It rises from zero to a sharp maximum at a distance of approximately one molecular diameter, and the size of the maximum usually corresponds to an average of about nine molecules in the "shell" of nearest neighbours, as opposed to twelve for close-packing. We should then expect a slight fall, followed by another rise corresponding to a possible nearly complete shell of next-nearest neighbours, and so on. In fact, our function is a "damped" version of that for a solid, and approaches a final value, corresponding to the equilibrium density of the liquid, after several oscillations of diminishing amplitude. Most of the features of the distribution function can be inferred from measurements on X-ray scattering, but some details remain doubtful, e.g., the form of its initial rise, as we go

out from the typical molecule, is difficult to infer with any accuracy.\* For some purposes, as we shall see later, the data from X-ray scattering can be used directly. Subject to small corrections, this gives us the three-dimensional Fourier transform of the distribution function, which is often more informative than the distribution function itself. This quantity never departs greatly from the pattern to be expected for simple rigid spheres. Consequently it has to be determined fairly accurately to be of any real use.

The accurate distribution function would tell us "nearly all that we want to know" about a classical liquid, in the sense that a knowledge of it at various temperatures and densities probably enables us to deduce, in principle, all the other thermodynamic and mechanical properties of the liquid. In the first place, deduction of the *equilibrium* properties is quite straightforward, given the usual assumption of additive, central, intermolecular forces. For the mean energy of interaction between a typical molecule and the remainder of the liquid, is, by the very definition of  $g(r)$ , equal to

$$\bar{\mathcal{V}} = \int_0^{\infty} dr r^2 g(r) V(r) / \int_0^{\infty} dr r^2 g(r) \quad (10)$$

and the total potential energy of the liquid is just  $\frac{1}{2}N$  times this. We have already shown that, for a classical liquid, (and, in certain circumstances, for a quantum liquid also) the mean kinetic energy per molecule is a known function of temperature, i.e., apart from possible internal degrees of freedom of the molecule, we know the total energy of the liquid, kinetic plus potential, as a function of density and temperature, from which the pressure and specific heats can be deduced by differentiation.

It is probable, but not yet quite certain, that the *transport* properties such as viscosity and heat conductivity are also fixed if  $g(r)$  and  $V(r)$  are given, and the liquid can be treated as classical. The arguments on which one bases this statement are extremely complicated and still contain gaps, but are probably correct, or nearly so. Very briefly, our object is to find some solution of the equations of motion of the molecules (or of equations, like Boltzmann's equation, that are deduced from them) that will correspond, for example, to the decay of the velocity gradient in a liquid that starts off by being uniformly sheared. To get a soluble, and physically meaningful, problem we seek the average rate of decay over a time that is long compared

\* Two atoms very close to one another would scatter radiation to high angles, and this is difficult to measure experimentally.

with the time between molecular collisions, the latter time being nearly always short compared with the "time of making an experimental measurement." (This may vary from a fraction of a second for an experiment on the absorption of ultrasonics to minutes or hours for a direct viscosity determination). The difficulty is to relate an average over a time lying between these two limits to averages over the possible configurations of the assembly (which regularly replace time averages in equilibrium statistical mechanics). Having made such a relation plausible, we have still to reckon with the fact that the time over which we average may be long in some such sense, but can not be a mathematical infinity. (Any assembly will reproduce its initial configuration, to any approximation, if we are prepared to wait a sufficiently long time. All irreversible effects therefore disappear if we average over *infinite* times.) These difficulties of principle are still far from settled, but the main outlines of the theory of irreversible processes seem to be well established, in the sense that we know, almost for certain, the quantities that we have to calculate, but methods of doing so are still crude.

Thus, it is natural that much attention should have been paid to the problem of computing the distribution function of a liquid of given density, if the interaction energy be supposed known as a function of distance, and various approximate methods have been devised. Unfortunately, the distribution function never differs very much from that appropriate to a liquid of nonattracting rigid spheres, attractive forces, or changes in the repulsive forces, producing only minor changes in the calculated pattern. Conversely, to predict the properties of the liquid properly, we require an extremely accurate knowledge of the distribution function. For example, if we wish to calculate the pressure of a liquid the kinetic term  $NkT/V$ , arising from the kinetic energy, and the term arising from the variation with volume of the mean potential energy (10) are nearly equal and of opposite sign, so that any inaccuracy in  $g(r)$  will be much magnified in an isotherm calculated from it. Similarly, it turns out that the calculated transport coefficients are extremely sensitive to variations of  $g(r)$ . We recall that a very similar situation exists in the van der Waal gas, the isotherm for which may be written as the difference of two terms

$$P = \frac{NkT}{V - b} - \frac{a}{V^2}$$

which essentially arise from the kinetic and potential energies of the molecules. It seems to be a fundamental property of the liquid state that these terms should be opposed and nearly equal. (If the attractive energy were large

compared with the kinetic energy we should have a solid; if it were small, we should have a vapour, i.e., the liquid would not hold together at all.)

The methods at present available for computing the distribution function are still rather tentative, and, while the *direct* comparison of "calculated" and "observed" distribution function is fairly satisfactory, the more sensitive checks provided by the equilibrium and transport properties give "order of magnitude" agreement only, as is to be expected from the above discussion.

## 2.2 Models Based on Quantum Considerations From the Start

So far, our discussion has been based on models involving essentially classical conceptions, but some of these can readily be extended to quantum assemblies. We now introduce some models using quantum conceptions from the start.

### 2.2.1 The Debye-Landau Model

This is really based on the experimental fact that a liquid can propagate sound waves with very little attenuation or dispersion. (As the frequency moves outside the range accessible to ultrasonics, it becomes likely, for a number of reasons, that both absorption and dispersion occur.) This suggests that we try to represent the thermal agitation of a solid or liquid by superposing sound waves. In other words, we compute the possible modes of a block of liquid or solid and argue that, in the long run, a mode of given frequency will be present with a certain amplitude. The amplitude of any mode is determined by the fact that the energy in that mode is given by Planck's function, so that the total energy lying in a frequency range between  $\nu$  and  $\nu + d\nu$  is

$$g(\nu) \frac{h\nu}{\exp(h\nu/kT) - 1} + \frac{1}{2} h\nu d\nu$$

and we can calculate the energy and other properties of the assembly if we know, or can guess,  $g(\nu)$  as a function of frequency. If it were possible to neglect dispersion, we should have the well-known expression

$$g(\nu) = 4\pi\nu^2 \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right)$$

$c_l$  and  $c_t$  being the velocities of propagation of compression and shear waves. Using this, we can take some account of the discontinuous structure of matter by introducing a cutoff frequency, so chosen that the total number



of modes is equal to  $3N$ , the correct number of degrees of freedom for an assembly of  $N$  molecules. More refined calculations, on simple models of a solid, lead to more complicated variations of  $g(\nu)$  with  $\nu$ , but do not change the over-all qualitative picture.

It is perhaps not obvious why Planck's function, originally deduced for a radiation field, should apply, almost without alteration, to the very different case of a sound field. It can, in fact, be shown that this treatment would be rigorously correct for the so-called "Hooke's law solid" in which the energy is a quadratic function of the displacements of the molecules from some standard configuration. Consider, for simplicity, the "one-dimensional ring solid," with interactions between nearest neighbours only. The potential energy is

$$V = V_0 \sum (x_r - x_{r+1})^2$$

and the Schrödinger equation is

$$\left( \frac{h^2}{8\pi^2m} \sum \frac{\partial^2}{\partial x_r^2} + E - V_0 \sum (x_r - x_{r+1})^2 \right) \psi = 0, \quad x_{n+1} \equiv x_1$$

If we put  $C_s = \sum x_r \cos(r\pi s/N)$ ,  $S_s = \sum x_r \sin(r\pi s/N)$  this equation separates into wave equations of simple harmonic oscillator type, with the same boundary condition that applies to a single particle, namely, that the wave function must vanish when the coordinate  $C_s$  or  $S_s$  becomes large. The possible eigenvalues of the problem are known to be  $\frac{1}{2}h\nu_s$ ,  $\frac{3}{2}h\nu_s$ , etc., and summing the corresponding Boltzmann factors leads to the Planck function in this case also. Even this very simple model leads to a dispersion of sound (velocity a function of frequency), and to a cutoff frequency above which no such excitations are possible.

This is for a solid. The main problem in adapting this work to apply to a liquid is to decide what replaces the transverse elastic waves in a solid. The longitudinal (compression) waves present no problem, as such sound waves can be propagated in a simple liquid at all experimentally accessible frequencies, and we can treat them in exactly the same way as in a solid. It is not experimentally possible to propagate transverse elastic waves in a simple liquid but it is, nevertheless, possible that they exist. The frequencies that one is most interested in for the Debye theory are of order of magnitude  $hT/h \approx 10^{11} - 10^{12}$ , which is far outside the experimental range. Various attempts were made, by optical scattering experiments, to look for these excitations, but the results were inconclusive. Therefore the situation is

very much less satisfactory than for a solid, for which one can actually measure the elastic constants and the velocities of propagation of elastic waves. For the liquid, we cannot measure the rigidity modulus, so the value we insert for the transverse sound velocity is little more than a guess. It is, of course always possible to analyze a specific heat curve in terms of an "effective Debye temperature," and to plot the variation of this quantity with temperature, but, with our uncertainty about the physics, it is difficult to assign any real meaning to such a plot for a liquid, whereas it can give much information about a solid.

A quite different point of view about these "transverse degrees of freedom" is due to Landau.<sup>1</sup> He was originally led to it by an attempt to quantize the equations of hydrodynamics by introducing *commutation relations* between the field quantities, resembling those occurring in quantum electrodynamics. If this were done correctly, or nearly correctly, it should be possible to discuss "idealized experiments" for measuring, e.g., density and current flow, and to decide what pairs of quantities can, in principle, be measured without mutual disturbance, and so be described by commuting operators (Vol. I, Chapter 2, § 3.3), and what pairs are analogous to position and momentum in particle dynamics, and have to be described by non-commuting operators. Furthermore, it ought to be possible to show whether the formalism is or is not consistent with the Schrödinger many-body wave equation. Neither of these investigations seems to have ever been made, so the validity or otherwise of Landau's treatment remains unsettled.

Landau's conclusions are, to a large extent, independent of the formalism. His picture of a liquid is that the excitations from the ground state consist partly of "phonons," i.e., sound waves, quantized in the way described above, which must be nearly correct as long as the amplitudes are not too large. He originally thought that the transverse sound waves should be replaced by *quantized vortices* or "rotons." Evidence has indeed been recently found for the existence of *vortex filaments* in the low temperature modification of liquid helium, as predicted by Onsager and Feynman, but the excitations usually referred to as "rotons" seem to be rather different. They are probably always present in the liquid to some extent, but vortex filaments tend to *decay*. The "rotons" probably represent states of motion of the liquid involving comparatively few molecules at a time — one can think of one molecule moving through the liquid and pushing the others aside, in a manner similar to the well-known motion of a solid sphere through a liquid as described by elementary hydrodynamics. The spectrum of such excitations is hard to predict quantitatively, and it is usual to choose it to get agreement with the observed specific heat. The combined spectrum required to do this,

if we ignore the distinction between phonons and rotons, is very similar in general form to the excitation spectra calculated for simple solids, probably going through two maxima and a minimum as the frequency increases. A sound wave necessarily involves the motion of a great many molecules, while the motion of a single molecule through the liquid might be expected to involve only a few others, but this qualitative distinction cannot be expected to hold at all frequencies, and it is not, strictly, possible to say that part of the spectrum consists of phonons and part of rotons; they seem to merge into one another. (In the elastic solid, it is also not possible, in general, to separate the normal modes into wholly transverse and wholly longitudinal.)

Clearly it is always possible to devise a spectrum of excitations that will represent almost any data, since we have so little to guide us apart from the measured velocity of sound in the liquid. Theoretically, the longitudinal waves should use up  $N$  degrees of freedom, leaving us  $2N$  others almost completely arbitrary. The complete determination of the spectrum seems to have been carried out only for liquid helium, where there is considerable evidence available that does not exist for other liquids.

### 2.2.2 The "Imperfect Quantum Mechanical Gas"

We have just discussed a modification of a solid model. The successes of the van der Waals model based on the idea of an imperfect but classical gas lead us to try the effect of correcting the perfect quantum mechanical gas by introducing "interaction" terms.

The *perfect* quantum mechanical gas can be treated fairly easily. Instead of trying to enumerate the energy levels of the whole assembly, it is simpler to enumerate those of one molecule at a time. For a cubical box of side  $d$ , the possible wave functions for one molecule are

$$\sin \left( \frac{p\pi x}{d} \right) \sin \left( \frac{q\pi y}{d} \right) \sin \left( \frac{r\pi z}{d} \right)$$

where  $p, q, r$ , are integers and the corresponding energy levels are

$$\hbar^2(p^2 + q^2 + r^2)/8md^2 = E_{p,q,r}.$$

In quantum mechanics we regard the molecules as indistinguishable so that we distinguish between states in which these levels are occupied a different number of times but pay no attention to interchanges between molecules. If a level  $(p,q,r)$  is occupied by  $n$  molecules, the Boltzmann factor is  $\exp(-nE_{p,q,r}/kT)$ . If the molecules are described by symmetrical wave functions  $n$  may take any value from zero upwards, and so the level

$(p, q, r)$  corresponds to a factor  $\sum_n \exp(-nE_{p,q,r}/kT)$  in the partition function, so that the complete partition function is

$$f = \prod_{p,q,r} \left\{ 1 + \lambda \exp \frac{h^2(p^2 + q^2 + r^2)}{8md^2kT} \right\}^{-1} \quad (12)$$

from which we have to select the coefficient of  $\lambda^N$ , where  $N$  is the total number of molecules. If, however, the molecules have a resultant half integral spin, as a result of being made up of an odd total number of protons, neutrons, and electrons, such molecules must be described by antisymmetrical wave functions and this implies, among other things, that each elementary level described above can each be occupied in only four distinct ways, if the molecules have a resultant spin of  $\frac{1}{2}$ . The level can be empty, or it can contain one molecule spin up or spin down, or it can contain two molecules of opposite spin. In such a case, (12) must be replaced by

$$f = \prod_{p,q,r} \left\{ 1 + \lambda \exp \left[ \frac{h^2(p^2 + q^2 + r^2)}{8md^2kT} \right] \right\}^4 \quad (13)$$

(13) is identical with the expression for the partition function of free electrons in a metal, on which the Sommerfeld model is based. A sufficiently good evaluation of expression (12) can be obtained by the artifice of taking logarithms, so as to reduce the product to a sum over  $p, q, r$ , expanding in powers of the exponential, and then replacing the summation over  $p, q, r$  by integrations. At very low temperatures this becomes inaccurate, but, in all cases, we get a sufficiently good answer if we retain explicitly the term corresponding to  $p = q = r = 1$ , the final result being

$$\log f = -\log \left| 1 - \lambda \exp \frac{3h^2}{8md^2kT} \right| + \left( \frac{2\pi md^2kT}{h^2} \right)^{3/2} \sum_{s=1}^{\infty} \lambda^s s^{-5/2}. \quad (14)$$

The evaluation of expression (13) has to be considered separately for various possible ranges of the parameter  $\lambda$ , but this problem has already cropped up in the theory of metals.

Expression (14) has some interesting properties. Clearly the argument of the logarithm must be positive, and this implies that the series always converges. According to the ordinary formulas of statistical mechanics,  $\lambda$  is related to the number of molecules in the assembly by  $N = \lambda [\partial(\log f)/\partial \lambda]$  and we get

$$N = \frac{\lambda \exp(3h^2/8md^2kT)}{1 - \lambda \exp(3h^2/8md^2kT)} + V \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \sum_{s=1}^{\infty} \lambda^s s^{-3/2}. \quad (15)$$

We notice that the series converges in all interesting cases in this expression also, because  $\lambda$  cannot exceed unity without making the first term negative. For  $d$  and  $V$  large, the exponential in (15) is very nearly unity. For  $\lambda = 1$  the sum of the series in (15) is 2.612... so that, for  $N/V$  greater than 2.612  $(2\pi mkT)^{3/2}/h^3$ , the first term in (15) becomes significant, whereas, as soon as  $\lambda$  falls appreciably below unity, this term is small compared with  $N$ .

The physical meaning of this result is that, for  $N/V$  greater than a certain value, or, for a given  $N/V$  and  $T$  below a certain value, even a completely perfect gas, without any interactions between the molecules at all, would show a peculiar condensation phenomenon, the very lowest level ( $p = q = r = 1$ ) containing a finite fraction of all the molecules, this fraction increasing if the temperature falls still further.\* This phenomenon is known as *Bose-Einstein condensation*. One might at first think that it has some connection with the liquefaction of a gas, but insertion of numbers shows that this transition occurs well below the solidification point of most substances, so little notice was taken of it. In 1938, however, F. London suggested that this transition might be connected with the transition of liquid helium that we shall be discussing below.<sup>4</sup>

Many attempts were made to allow for the interactions between real molecules by such devices as modifying the spectrum of energy levels, or introducing terms of van der Waals' type, to try and make a theory of a "quantum liquid," with much the same results as for other liquid models, namely that certain results could be reproduced quantitatively, and others predicted in order of magnitude. In practice, most of such work has been directed towards efforts to explain the properties of liquid  $\text{He}_4$ , since interactions are weak and the atoms are light, so we might expect quantum effects to be more marked than in other liquids. Various attempts have also been made to modify the accepted treatment of electrons in metals (Fermi gas) so as to obtain a model of liquid  $\text{He}_3$ , and the experience there has been much the same. This much is quite clear, there are marked differences between the two liquids, far more fundamental than can be accounted for by differences of interaction or mass, and they can be partially explained on the basis that there is a fundamental difference between the wave func-

\* We have used rather "rough and ready" mathematics to arrive at this result but a number of more refined investigations have confirmed its validity. For example, it makes no difference if we separate off a band of the very lowest levels and study them separately. It is well known to mathematicians, that, if we approximate to a series by an integral, we sometimes have to take explicit account of the first and last terms, and this is what occurs here.

tions describing  $\text{He}_3$  and  $\text{He}_4$  atoms. Thus we have fresh confirmation of the validity of deductions based on the symmetry properties of wave functions. This was one of the essentially new ideas introduced by wave mechanics into the quantum theory.

### 2.2.3 The "Pair" Model

One way in which we might attempt a theory of a liquid would be on the lines of a Hartree (Chapter 2, § 13.3, in this volume) or Fermi-Thomas (Chapter 5, § 3.2, in this volume) type of "self-consistent field" calculation; that is, we think of our liquid as one vast molecule, and try to find reasonable wave functions which shall describe the motion of a typical atom in some kind of "smoothed field." This wave function also tells us the probability of finding atoms at any given point, and we would go on adjusting our wave function until the smoothed field was consistent both with this variation of density from point to point, and also with the interaction function, assumed known. Such a programme never actually seems to have been carried out for any realistic case, in spite of the fact that it would certainly be a better approximation to the actual situation in a liquid than crude models of the "cell" or "hole" type. One reason for this omission is that a "self-consistent" calculation would still be rather a poor approximation (the motion of many particles cannot be described properly in terms of that of one typical particle). For example, we have nothing corresponding to the distribution function for describing the "correlations of distance" that *must* exist between any two typical particles because of their interactions.

Very recently, a more ambitious programme has been tried by Brueckner and others,<sup>5</sup> with the object of describing nuclear matter (which probably resembles a liquid in many respects), and also liquids like helium and hydrogen where quantum effects are likely to be important. Very briefly, their method is as follows. A typical *pair* of particles is thought of as moving in a "smoothed potential" representing their interactions with the remaining  $N - 2$  particles, and the interaction between the two particles is allowed for explicitly. Assuming, for the moment, that the smoothed potential is known, it is a soluble problem to determine wave functions for the two particles that takes explicit account of their symmetry properties, and these wave functions are then used to adjust the smoothed potential, on the same principles as in ordinary "self-consistent" calculations. The other refinement is that the smoothed potential is not now simply a *scalar*, but an *operator*. We are familiar with operators appearing in the Dirac wave equation or in the Schrödinger equation with a magnetic field (Vol. I, Chapter 8, § 5.1.4). In practice, the effect is the same here — the interaction of a particle with

the smoothed potential depending not only on its position, but also on its velocity and its spin function. A dependence of the "smoothed potential" on velocity is extremely reasonable in a liquid, if for no other reason than that the distribution of particles "seen" by one particular one moving through the liquid will not, in general, be independent of the velocity. For a slow particle, there is more time for the rest of the structure to adjust itself to its motion than there is for a fast one. In simple versions of the model we can either guess a smoothed potential such as a constant potential, or even more crudely, we can guess the form of the "pair" energy levels. A genuine "self-consistent" treatment must clearly include some way of determining, from the wave function, the operator representing the smoothed potential. Anything of this kind must be fairly elaborate and on a much bigger scale than a Hartree type calculation. Since the latter is already near the limit of what can be efficiently done by hand-computing, it follows that the Brueckner method is essentially one for a large automatic computer. It has already been applied to nuclear matter and liquid  $\text{He}_3$  with promising results. Its application to symmetrical assemblies like  $\text{He}_4$  is more difficult. Investigation has shown that certain cancellations of errors that fortunately occur in the antisymmetrical case do not do so in the symmetrical one, and an *attractive* interaction proves difficult to handle.

### 2.3 Attempts to "Quantize" Purely Classical Models

A simple approach to some problems begins with one of the purely classical conceptions like the "cell" model by asking how it might be affected if we leave our smoothed potential unaltered, but work out the resulting energy levels quantum mechanically, instead of classically. Apart from symmetry effects, which *cannot* be dealt with properly by such a one-particle treatment, there are two other possibilities worth considering. In the first place, are we ever likely to meet conditions in which the "tunnel effect" is of significance? In other words, does a typical molecule ever leak out of its cell even though it has not enough energy to overcome the potential barrier surrounding the cell? One might further look for effects analogous to those occurring in metals, corresponding to the existence of allowed and forbidden bands of energy, that may be expected to be the result of a spatially periodic field. The short answer to such questions is that such effects are quite possible, but would be extremely difficult to verify. Classically, there is always a finite probability that a molecule can escape from its cell, its neighbours moving aside to let it through. On this basis it is possible to account qualitatively for viscosity and diffusion and thermal conductivity,

on the basis that this "probability of escape" will vary slightly from place to place if there is a gradient in temperature, pressure or density. A quantum mechanical calculation could only *modify* this probability of escape, which is usually an adjustable parameter in any case.

### 2.3.1 Zero-Point Energy

There is an effect that is completely absent in the classical liquid that can be of considerable importance, namely the zero-point energy. The order of magnitude of this can easily be computed, but, even for a very simple model in which molecules are represented by nonattracting rigid spheres, the detailed variation with density is still not known accurately. For a "cell" model, if  $d$  is the maximum dimension of a cell, the energy of the lowest possible energy level for one molecule is of the order of magnitude of  $h^2/md^2$ . Now, we should expect  $d^3$  to vary inversely with density in a rarefied assembly, in which the volume of a cell is roughly the same as the "share" of the "free volume,"  $v - b$  of the assembly available ( $b$  is the van der Waals constant) to any one atom, whereas, in an assembly of nearly rigid molecules approaching close packing, we should expect  $d$  to approach a constant value comparable with  $\sigma$ , the gas kinetic diameter. In this region, however, the increase of zero-point energy does not cease. As the molecules are squeezed nearer to one another, it becomes more and more difficult for our specimen molecule to escape from between its neighbours either classically or by virtue of the tunnel effect, and we can describe this by saying that not only is the cell becoming smaller, but the height of the potential barriers surrounding it is going up, and both these effects have to be considered. Qualitatively, we can say that, over a reasonably range of densities, the zero-point energy should increase with a fairly low inverse power of the density, probably of the order of two or three.

The zero-point energy can be roughly estimated from a Debye-like model also. An interaction like that given by (11) binds a typical molecule to the neighbourhood of the centre of gravity of its neighbours. This interaction is intended to represent the effect of intermolecular forces, and is assumed to be of parabolic (or Hooke's law) form to obtain a model that can be solved completely. According to this model, the zero-point energy arises from the term  $\frac{1}{2}h\nu$  for the lowest level of each of the virtual oscillators into which our assembly is decomposed. It arises for just the same reason as the zero-point energy in the cell model, namely, it is a measure of the confinement of a typical molecule by the interactions of neighbours. For the simple "Debye solid," summation over all the oscillators gives an estimate  $9Nk\Theta/8$ , where  $\Theta$  is the Debye temperature. It is possible to derive a Debye tem-



perature of a liquid by measuring its specific heat, but the difficulties associated with the transverse degrees of freedom already discussed mean that only an "order of magnitude" reliance is to be put on the zero point energy measured in this fashion — the theoretical backing for the Debye model being much less satisfactory in the liquid than it is in the solid. This approach again predicts a zero-point energy that increases as a fairly low power of the density. We now deduce some physical consequences of the existence of this energy.

In the first place, if it varies with density, as it always will, we get a "quantum" contribution to the pressure. This occurs simply because, if we compress the liquid, its zero-point energy is increased, quite apart from any increase of the *direct* interactions between the molecules. All that we have to do is to include the zero-point energy in the thermodynamic internal energy function and an extra term in the pressure then appears when we differentiate with respect to volume. (The reader will easily verify that this is dimensionally in accord with de Boer's extension of the principle of corresponding states already discussed.) The zero-point energy is kinetic, since it arises from the *confinement* of typical molecules which is only indirectly a result of their interactions, and it is sometimes kept separate from the "ordinary" increase in kinetic energy that occurs when the temperature rises. Strictly speaking, the latter increase occurs because the assembly now has a chance of occupying states other than the ground state, and it is not really correct to separate the total kinetic energy of such an excited state into "zero-point" and "thermal" parts, though such a division may be convenient. For the Debye model at low temperatures, this leads to  $E = E_0 + AT^4 + \dots$

Another quantum departure from a "corresponding states" type of behaviour occurs when a liquid of light molecules evaporates. The zero-point energy is definitely present in the liquid but absent in the vapour, and this means that our observed latent heat of evaporation is lower than we might expect. This leads to a departure from Trouton's rule, which was discovered empirically but has a fairly sound theoretical basis, namely that, if a liquid is evaporated at its boiling point  $L/T$  is practically the same for all liquids, of the order of 20–25 cal/deg/mole. The theoretical basis of this is that the thermodynamic behaviour of vapours is surprisingly close to that of perfect gases, so that the entropy of the vapour exceeds that of the liquid by roughly  $Nk \log [V(\text{vapour})/V(\text{liquid})]$ , the internal degrees of freedom of the molecule not concerning us here, because they are not greatly affected by evaporation. Thus, for substances that roughly obey the law of corresponding states the ratio of densities of liquid and vapour depends only on the reduced temperature and, because of the logarithm, the entropy of evaporation is

nearly constant which leads to Trouton's rule. The argument still holds for quantum liquids, because the vapour can still be treated as classical and the entropy of the liquid is negligible compared with that of the vapour, but "work is now done by the zero-point pressure," i.e., the zero-point energy disappears as the liquid expands into vapour, and a smaller latent heat is needed in order to lead to the same entropy change. Trouton's rule is rather rough, so it is only with liquids like helium and hydrogen that we can detect departures from it with certainty. For  $\text{He}_4$ , the effect is very important, we expect a latent heat of the order of 80–100 cal/mole and only observe 14 cal/mole, the rest being due to the zero-point energy. That is to say, that, in this liquid this typically quantum effect plays a major part in determining the equation of state.

One result of this is that the density is much lower than we might expect. In an "ordinary" liquid, the intermolecular distance corresponds to a rough balance between the attractive and repulsive forces between a typical pair of neighbours, whereas liquid helium is "blown out" by the zero-point effect to a density only about one third of what we might expect on a classical basis. Thus, this liquid is already giving us evidence of the importance of quantum effects. The repulsive forces play little direct part in fixing the equilibrium density, instead we have a rough balance between the "zero-point pressure" and the attractive forces, or speaking more precisely, the liquid adjusts itself to near the region of minimum total energy. We can, if we like, compare the liquid with the deuteron nucleus. With this system we have two heavy particles bound by a short range interaction that is only just enough to give us a bound level. As a result, the net binding energy is very small, and the wave function remains appreciable out to distances several times the range of action of the nuclear forces. The same is true of two helium atoms, the interaction between them is probably about enough to give a bound state when two atoms interact. We can thus expect to find some points of resemblance between helium, particularly  $\text{He}_3$ , and nuclear matter (Vol. III, Chapter 5).

One very interesting consequence of the zero-point energy is that neither form of helium solidifies at atmospheric pressure, but requires an external pressure of at least 25–30 atm. The relationship between interaction forces and the type of crystal lattice that results from them, and, in particular, the circumstances in which it is profitable to form an ordered lattice rather than a random one, are not properly understood. A fairly delicate balance is probably involved in most cases, since the calculated differences in energy between various lattice structures are always fairly small, and the energy and entropy of a disordered structure cannot yet be calculated with enough

accuracy for comparison. The large zero-point energy term far exceeds the small differences between the energies of various possible structures, so it is not surprising that the situation is quite different from that in an ordinary solid.

### 2.3.2 *Distribution Function*

Since the distribution function technique looks so promising in the classical case, and since it involves concepts like the probability of finding one molecule at a given distance from another which figure so often in quantum mechanical investigations, it is only natural to look for a generalization of the work. In one sense, one can perhaps regard Brueckner's<sup>5</sup> work, in which the interaction of two molecules is considered explicitly and the effect of the remainder is "smeared out" as being this generalization. In classical distribution function theory an approximation in the same spirit, the so-called Kirkwood or "superposition" approximation is necessary in order to make any real progress. One suggestion has been to replace the distribution function by the density matrix and try to find a satisfactory form for that. Although the equation it satisfies is apparently quite simple, it is difficult to formulate properly the boundary conditions it must satisfy. An approximate treatment by Born and Green<sup>6</sup> is practically equivalent to treating a typical pair as moving in a constant "smoothed potential." The problem then reduces to the soluble one of the motion of two molecules under the influence of their interaction, and the two-molecule distribution function reduces to the probability of finding the two molecules at various distances, due regard being paid to their symmetry properties. Their theory did indeed predict a large difference between the properties of the two isotopes of helium, but gave quite wrong predictions for the distribution function of  $\text{He}_4$  at low temperatures, seeming to show that the above assumption is an over-simplification.

## 2.4 Direct Attacks on the Quantum Mechanical, Many-Body Problem

Since treatments based on tentative models tend to contain too many adjustable parameters, and since attempts to find quantum mechanical versions of classical hydrodynamics or sound theory must ultimately lead us back to the many body problem for their formal justification, one is naturally led to ask whether anything can be deduced from a direct study of the many-body problem itself. In fact, progress has been made in two quite distinct directions.

### 2.4.1 The Bijl Transformation

The idea here is particularly suitable for very low temperatures. We assume that we know the exact wave function of the very lowest state of the liquid, and we look for other solutions of the many-body wave equation, of the approximate form

$$\psi = \phi \psi_0$$

where  $\psi_0$  is the ground-state wave function. Substituting this into the many-body wave equation, and using the fact that  $\psi_0$  is a solution of it, we can get an equation in which the troublesome interaction potential does not appear directly

$$\frac{\hbar^2}{8\pi^2m} \left( \sum \nabla_n^2 \phi + \frac{2}{\psi_0} \sum \nabla_n \psi_0 \cdot \nabla_n \phi \right) + (E - E_0) \phi = 0. \quad (16)$$

In actual fact, we know very little about  $\psi_0$ , which has never been worked out for any realistic interaction, but, for our present purposes, we only need some very general properties, namely that, being the ground state wave function,  $\psi_0$  may be expected to be real, and to be without nodes. In other words, no configuration of the molecules in the vessel is actually forbidden, but those in which, e.g., two molecules are very near one another correspond to very small values of the wave function, which is largest for configurations in which the interaction energy is lowest, which will be those in which the atoms are spaced nearly uniformly.

Equation (16) may also be written, if we choose our energy zero so that  $E_0 = 0$

$$E \psi_0^2 \phi = \frac{\hbar^2}{8\pi^2m} \sum \nabla_n \cdot (\psi_0^2 \nabla_n \phi)$$

Now multiply both sides by  $\phi^*$ , integrate over all the coordinates of all the atoms, and apply Green's theorem to the right-hand side, remembering that  $\psi_0$  must vanish whenever any one of the molecules is on the walls of the vessel, so that the surface integrals all vanish

$$E \int_{(n)} \psi_0^2 \phi \phi^* d\tau_n = \frac{\hbar^2}{8\pi^2m} \int_{(n)} \psi_0^2 \sum_n \nabla_n \phi \cdot \nabla_n \phi^* d\tau_n, \quad (17)$$

$d\tau_n$  standing for the product of the volume elements for the  $n$  sets of coordinates.

Equation (17) is exact, but to make further progress we have to assume some form for the function  $\phi$ . We know that when making calculations of

energy levels, fairly crude approximations to the wave function often give quite good results (Vol. I, Chapter 6, § 3.1). Also, because of symmetry requirements our new wave function, and therefore  $\phi$ , must be a symmetrical function of the coordinates of all the atoms, so that we are led to try as the simplest possibility, a function of the type  $\phi = \sum_n f(x_n, y_n, z_n)$ . By a variational argument, we can show that the form of  $f$  that leads to the lowest energy is a function of the type  $\exp(i\mathbf{k} \cdot \mathbf{x})$ , which is therefore the "best-possible" choice of wave function with this type of  $\phi$ . It is possible to give physical arguments to show that this proposed wave function does in fact give a reasonable description of simple situations in the liquid, such as the motion of one molecule and the consequential displacements of others near its path, so it should lead to reasonable results for the energy.

Substituting this function into (17), we find, for the left-hand side,

$$\int \psi_0^2 \sum_{i,j} e^{i\mathbf{k} \cdot (\mathbf{x}_i - \mathbf{x}_j)} d\tau_n.$$

We can take  $i$  and  $j$  to refer to different molecules, because  $\psi_0$  is extremely small if two molecules coincide. For any choice of  $i$  and  $j$  we can integrate over the coordinates of all the molecules except  $i$  and  $j$  remembering that  $\psi_0^2$  is, by definition, proportional to the probability that molecule 1 will be found near  $(x_1, y_1, z_1)$ , and at the same time molecule 2 near  $(x_2, y_2, z_2)$ , etc. After integration over the coordinates of all but two of the molecules, we are left with  $\frac{1}{2}N(N-1)$  terms of the type

$$V^{N-2} E \int g(r_{ij}) \exp(i\mathbf{k} \cdot \mathbf{x}_{ij}) d\tau_i d\tau_j,$$

because  $g(r_{ij})$  is, by definition, proportional to the probability of finding two specified atoms at a distance apart  $r_{ij}$ , and is the result of integrating  $\psi_0^2$  over the coordinates of all but two of the molecules. Neglecting wall effects this probability depends only on the distance apart of these two molecules, and not at all on their absolute positions, so that the integration over the coordinates of one molecule leads simply to a factor  $V$ . Further,  $g(r_{ij})$  is independent of the direction of  $r_{ij}$  in space, so we may integrate over the polar angles. Thus the left-hand side of (17) reduces to

$$\frac{1}{2}V^{N-1}EN^2S(k)$$

where  $S(k)$  is equal to  $4\pi \int_0^\infty g(r)e^{i\mathbf{k} \cdot \mathbf{r}} r^2 dr$ , the three-dimensional Fourier transform of the distribution function, which depends only on  $k$ , the magnitude of  $\mathbf{k}$ . With this same choice of  $\phi$ , the sum on the right-hand side

of (17) reduces simply to a factor  $Nk^2$ , and the result of integrating  $\psi_0^2$  over the coordinates of all the molecules leads, by definition, to a probability of unity, i.e., the right-hand side is  $Nk^2V^N$ , so that we have, finally, as our estimated energy of an excited level

$$E(k) = \frac{\hbar^2 k^2}{4\pi^2 m} \frac{V}{NS(k)} \quad (18)$$

which also depends only on the magnitude of  $k$ .

Thus, we can make an estimate of the distribution of the energy levels above the ground state if we know  $g(r)$ , the distribution function. This treatment thus bypasses the difficult problem of computing the many-body wave functions associated with our interaction; we can, instead, take  $g(r)$  as the datum which is to be fed into the theory. Actually, nature is particularly obliging on this occasion, because what we really require is  $S(k)$ , and it is effectively this quantity that we actually measure when we make an X-ray or neutron diffraction study of a liquid, a maximum in  $S(k)$  as a function of  $k$  corresponding to a diffraction ring.  $S(k)$  is linear for small  $k$  in a liquid, so that  $E(k)$  is also linear, and the spectrum of the energy levels of a liquid resembles that of a solid, being linear with wave number for small wave numbers and going through maxima and minima following the variation of  $S(k)$ . Thus, we are led to expect a "Debye-like" spectrum for a liquid very similar to that for a solid, *even though the arguments that lead to them are completely different, and the form of the wave functions is also completely different*. So, again, we are in difficulty when we try to confirm our predictions experimentally. Even though we arrive at a spectrum of excitations that agrees with experiment, e.g., with the observed specific heat, it is *not* a valid deduction from this that we have been using a nearly correct wave function. At present any decision between the solidlike approach and the present one must rest on physical arguments. For liquid helium, the solidlike approach is particularly unconvincing, because of the big effect of the zero-point energy, and the present treatment is probably preferable. For other liquids, for which the density is not much greater than that for close-packing of the molecules, the position is less clear.

#### 2.4.2 The Bohm-Pines Transformation

This treatment was originally designed for the description of a *plasma*, or, of other systems of electric charges interacting through Coulomb interactions, for which it has been extremely valuable. It is, however, quite general and is at least formally applicable to other many-body problems, but,

as we shall see, it has to be used with care if the interactions between the molecules are of "hard-core" type. We shall first carry out the treatment for a *classical* assembly with a general interaction, and we shall then indicate how a quantum mechanical treatment can be developed, though the details rapidly become complicated.

The transformation used is quite simple, namely we use new "coordinates"  $q_k$ , related to the coordinates of the particles themselves by

$$q_k = \sum e^{-i\mathbf{k} \cdot \mathbf{x}_i} \quad (19)$$

These quantities are, in fact, the Fourier components of the total "particle density," which is expressed in terms of Dirac delta functions, without any attempt being made to smooth them off into a continuous function. That is, the particles are treated as separate points rather than as a continuous distribution. Thus, we have for the charge density

$$\rho(\mathbf{x}) = \sum_i \delta(\mathbf{x} - \mathbf{x}_i) = \sum_{i,k} e^{i\mathbf{k} \cdot (\mathbf{x} - \mathbf{x}_i)}$$

for unit volume. Assume, as usual, that the interaction potential between two particles is additive, central and nondirectional, and suppose the potential between any two particles analyzed into its Fourier components is

$$V(|\mathbf{x}_i - \mathbf{x}_j|) = \sum_k V_k e^{i\mathbf{k} \cdot (\mathbf{x}_i - \mathbf{x}_j)}$$

The equation of motion of any given particle is clearly

$$\frac{d^2 \mathbf{x}_i}{dt^2} = -\frac{1}{m} \sum_j \frac{\partial V_{ij}}{\partial \mathbf{x}_i} = -\frac{i}{m} \sum_{j,k} \mathbf{k} V_k e^{i\mathbf{k} \cdot (\mathbf{x}_i - \mathbf{x}_j)} \quad (20)$$

We use this to derive the equation of motion of the quantity  $q_k$ . We have

$$\frac{dq_k}{dt} = -i \sum_i \mathbf{k} \cdot \mathbf{U}_i e^{-i\mathbf{k} \cdot \mathbf{x}_i}$$

where  $\mathbf{U}_i$  is the velocity vector of the particle  $i$ . Differentiating again and using (20) for the acceleration, we find

$$\frac{d^2 q_k}{dt^2} = - \sum_i (\mathbf{k} \cdot \mathbf{U}_i)^2 e^{-i\mathbf{k} \cdot \mathbf{x}_i} - \sum_{l,j} \frac{V_l}{m} (\mathbf{k} \cdot \mathbf{l}) \exp [i(\mathbf{l} - \mathbf{k}) \cdot \mathbf{x}_i] \times \exp (-i\mathbf{l} \cdot \mathbf{x}_j) \quad (21)$$

where, in (20) we have replaced summation over  $k$  by summation over the similar variable  $l$ . So far this is exact (provided that the potential function can be validly analyzed into a three-dimensional Fourier series). The characteristic Bohm and Pines approximation is the "assumption of random phase," which consists of neglecting all terms in the  $l$  summation except those for which  $k = l$ . The summation over  $i$  then leads simply to a factor  $N$ , where  $N$  is the number of particles per unit volume, while the summation over  $j$  simply reproduces the variable  $q_k$ , so that we have

$$\frac{d^2 q_k}{dt^2} = \frac{N k^2 V_k}{m} q_k - \sum (\mathbf{k} \cdot \mathbf{U}_i)^2 e^{-i \mathbf{k} \cdot \mathbf{x}_i} \quad (22)$$

The assumption of random phase implies that, when  $l$  is significantly different from  $k$ , the oscillating terms from the exponential involving  $\mathbf{x}_i - \mathbf{x}_j$  may be expected to cancel one another out. (This is reasonable both for a plasma and a liquid, where there is no reason to expect correlations in the positions of two particles selected at random, but would not be valid, e.g., in a crystal lattice.) For the Coulomb interaction, it is possible to give other arguments. For this case, we have  $V_k = 4\pi e^2/k^2$ , and, for small  $k$ , we obtain from (22)  $\omega^2 = 4\pi N e^2/m$ , which is the well-known expression for the frequency of plasma oscillations. Since the second term of (22) is certainly small for small enough  $k$ , this agreement makes us confident that, at least in this region, the effects of the random-phase assumption are small also.

The Coulomb interaction is, of course, a special case, in that the characteristic frequencies are, to a first approximation, *independent of  $k$* , but this will not be so for other forms of  $V$ .

The treatment is clearly unsuitable for rigid spheres, or for any interaction involving a rigid core, since the decomposition into Fourier components is not possible. However, if  $V$  is finite at the origin of  $r$ , or if it goes to infinity more slowly than  $1/r$ ,  $V_k$  may approach a constant value as  $k \rightarrow 0$ , and we again get a Debye-like spectrum of frequencies, frequency being initially proportional to wave number, which corresponds to a "velocity of propagation" that is constant for small frequencies, which it is tempting to identify with the velocity of sound in the liquid. This is certainly an oversimplification as it makes the velocity of sound proportional to the square root of the density, irrespective of the form of  $V(r)$ , and also makes it depend on an integral  $\int_0^\infty r^2 V(r) dr$ , whereas, on physical grounds, one would give most weight to the behaviour of  $V(r)$  for  $r$  near the mean intermolecular distance. However, the argument is certainly right qualitatively, and once again, we arrive at a Debye-like spectrum of excitations for the liquid.



We have not yet considered the effect of the sum term in (22). Since it involves  $k$ , its effect is to introduce *dispersion*, so that  $\omega$  is no longer proportional to  $k$ . For Coulomb interactions and classical conditions, it can readily be shown, by successive approximation, that excitations of this kind cease to have a finite frequency for a wavelength corresponding roughly to the "Debye-Hückel distance," that is to say the distance to which the field of an individual charge is perceptible, before it is screened off by the rearrangement of other charges in the neighbourhood.

A similar length probably exists for other forms of the interaction function. Its physical meaning is that collective excitations involving the simultaneous motion of a great many of the atoms are not possible if the wavelength falls below a certain value. (In the Debye specific heat theory, based on sound waves, this limiting wavelength turned out to be comparable with the intermolecular distance.) For any interaction we are left with the question of the possible form of other types of excitation. A very interesting attempt to set up a *general* operator theory, analysing the many-body spectrum into collective and individual excitations has been made by Tomonaga.<sup>7</sup> His results are practically equivalent to those summarized above but are expressed in quantum language, in the place of the above "semiclassical" treatment. He justifies the separation of collective variables from the Hamiltonian by an argument almost exactly equivalent to the "random-phase" one. As we might expect, instead of using an "acceleration" equation like (22), the characteristic frequencies are derived from a Hamiltonian containing *differentiations* with respect to the variables  $q_k$ , but the results are practically the same.

We conclude this survey with a remark about the effect of splitting off the collective excitations from the Hamiltonian. We have seen that these are associated with the Fourier components  $V_k$  for which  $k$  is small, which are determined mainly by the behaviour of  $V(r)$  for  $r$  large. If we subtract out these  $V_k$ , we are left, in the Coulomb case, with a "screened" potential,  $1/r \exp(r/r_0)$ , vanishing at distances much greater than the Debye distance  $r_0$ . Thus, we might reasonably expect the remainder of the potential energy in the Hamiltonian to represent "quasi particles" with an effective interaction potential of only short range. However, it is not so easy to see that the remainder of the kinetic part of the Hamiltonian, involving differentiations with respect to the  $q_k$ 's, can be reduced to a correspondingly simple form if we omit all the  $q_k$ 's below a certain limit and retain the rest, but such a result is at least plausible (see Brenig<sup>8</sup>). If we assume it, this means that besides excitations resembling the sound waves in a liquid, we may expect excitations resembling the motion of free particles, except that their "effec-

tive mass" will probably differ from the mass of the molecules (because we have subtracted away part of the total kinetic energy in the Hamiltonian), and their effective interaction with other quasi particles will be small (because we have subtracted out the long range part of the interaction potential). Thus, the motion of one quasi particle probably only affects a few of the others.

Thus, by a quite different route, we have eventually arrived at the same sort of picture as that proposed by Landau and Feynman for a quantum liquid. "Phonons," or quantized sound waves of relatively long wavelength, each involving the motion of a great many atoms and "rotons" which probably resemble the motion of free particles, or only involve a few molecules at a time, and do not necessarily possess any vorticity.

### 3. The Properties of Liquid Helium

Since we have no satisfactory classical model of a liquid, we cannot hope for a quantitative theory of the corresponding quantum mechanical assembly. However, a study of the properties of liquid helium has been of value. Until we have some understanding of them, we can never exclude the possibility that we are omitting something important from the description of other liquids. Because of this, and because of the intrinsic interest of these properties, much work has been done and some of the theoretical effort described above was inspired by the existence of this liquid. We shall give a fairly brief review of the main experimental facts, and then show how most of them can be interpreted in the light of the theoretical ideas described above.

#### 3.1 The Diagram of State

The unusual features are, first, the existence of two forms of the liquid (for  $\text{He}_4$ ), and secondly, the persistence of the liquid phase down to absolute zero for both isotopes. We have seen that the latter circumstance can be accounted for qualitatively on the basis of solidification being hindered by the large zero-point energy. Each isotope has a peculiarity in the liquid-solid curve that is not properly understood. The solidification curve for  $\text{He}_3$  goes through a minimum pressure at about  $0.4^\circ \text{K}$ . This is probably connected with a magnetic transition in either liquid or solid at a slightly lower temperature, and there is a little evidence for this. The anomaly for  $\text{He}_4$  is more subtle, amounting to a change of sign of the difference in internal energy between solid and liquid, occurring at about  $1.6^\circ \text{K}$ . We have

$$\Delta U \approx T\Delta S - P\Delta V,$$

the two terms on the right-hand side both being positive, and  $P$  remaining finite as  $T \rightarrow 0$ . Above this temperature, the liquid has the higher internal energy as usual, but below this temperature, the external work done on melting more than balances the latent heat. This result is not completely understood, but it seems clear that it is another consequence of the high zero-point energy in both liquid and solid.

Much more spectacular is the transition of the liquid  $\text{He}_4$ . At vapour pressure this occurs at about  $2.18^\circ\text{K}$ . The specific heat probably becomes "infinite," but there is no measurable latent heat. These remarks hold good not only at vapour pressure, the transition line runs all the way between the vapour pressure and solidification curves, dividing the "liquid" region of the phase diagram into two portions. It was soon found that the low temperature form of the liquid had some very remarkable properties — the first one to attract attention being the fact that it does not "boil" by developing bubbles like an ordinary liquid, but evaporates steadily from the free surface. Further investigation suggested that the liquid was an extremely good heat conductor, perhaps analogous to a superconductor, but we now know that the true interpretation is much more complicated.

### 3.2 The Transport Properties of Liquid He II

When it was found that the apparent heat conductivity was not a constant, but varied in a most complicated fashion with the temperature gradient and the geometry of the measuring apparatus, efforts were made to measure other transport properties. Attempts to measure the viscosity of the liquid by "capillary tube" methods also produced a crop of nonlinear results, but did yield an important clue. Not only did it seem that the viscosity was extremely small numerically — the liquid penetrating with ease through channels formed by compressing jewellers rouge, estimated to be only about  $10^{-6}$  cm in lateral dimensions — but it seemed as if the concept itself required modification in some way, since, with a fine capillary, the rate of flow was almost independent of its length. However, attempts to measure the viscosity by an oscillating disk method seemed to give a finite viscosity, comparable numerically with that of He I. Now any "oscillation" measurement is theoretically capable of giving two quite separate pieces of information since we can measure, very accurately, both the damping and the change in period. Investigation shows that from this we can calculate both the viscosity and the effective density of the liquid "carried round" by the disk. (To get an easily measurable effect on the period one uses a pile of discs spaced along a rod rather than a single one, but this does not affect the principle of the method.) The experimental fact

is that the "effective density," measured in this way, is less than the actual density of the liquid. This, coupled with the anomalous results from the capillary tube method, suggested that part of the liquid might be *slipping along* solid surfaces. To be more specific, we suggest that part of the liquid is behaving as if it had very small viscosity and is capable of slipping over solid surfaces, while another part of the liquid seems to have a finite viscosity and to be dragged along by the movement of solid surfaces. This is known as the *two-fluid concept*. Although it seems highly artificial to think of anything so simple chemically as liquid helium as consisting of a solution or mixture of *two* fluids with such different properties, the concept *has* to be taken seriously. Not only does it collate a large number of experimental facts, but it soon proved itself capable of predicting others. Furthermore, as we shall see later, at least two of the models of the liquid described above *do* lead to the two-fluid picture. Thus, this strange concept satisfies all the requirements for being accepted as a physical reality, it is a consequence of a reasonable model and it is capable of interpreting experimental facts. The apparently very high heat conductivity, associated with non-linearity and dependence on geometry, suggests that we really are dealing with a *convection* effect.

### 3.3 The Two-Fluid Model

We suppose the viscosity and heat capacity of one fluid to be negligible, while the other behaves just like an ordinary liquid. We also suppose, as the oscillation experiments indicate, that the ratio of effective densities varies with temperature, and that each fluid has its own stream velocity vector, each of which may vary from point to point in the liquid, just like the stream velocity of ordinary hydrodynamics. We have now assumed a good deal more than is required by the viscosity experiments, and we must examine the consequences of these assumptions. In what follows the suffix *s* refers to the density and stream velocity of the superfluid while suffix *n* refers to the normal fluid.

Since the superfluid can penetrate through very narrow channels while the normal fluid is held back by its viscosity, and since the ratio of densities is a function of temperature, we should expect some phenomenon analogous to *osmotic pressure*, and this is observed. If two vessels containing liquid He II are separated by a narrow slit, or a pad of jeweller's rouge, and we maintain a difference of temperature between them, a pressure difference builds up, this being known as the *fountain effect*. Like all osmotic effects it is quite large, a pressure head of centimetres of liquid He corresponding

to a temperature difference of the order of 0.001 °K. We can predict the relationship thermodynamically. If we suppose a small mass of superfluid transferred from one vessel to the other, this can be regarded as a reversible process, since very little work is done against viscosity, and no entropy is transported by the superfluid. So the condition of equilibrium is that no net work is done by such a transfer, that is, that

$$\left(\frac{\partial E}{\partial m}\right)_{v,s} = \left(\frac{\partial G}{\partial m}\right)_{P,T} = g$$

is the same in both vessels. Thus, if  $\Delta P$  and  $\Delta T$  are the pressure and temperature differences

$$g(P,T) = g(P + \Delta P, T + \Delta T)$$

or

$$\frac{\Delta P}{\Delta T} = - \left( \frac{\partial g}{\partial T} \right)_P / \left( \frac{\partial g}{\partial P} \right)_T = \rho s \quad (23)$$

( $s$  is the entropy of unit mass of the liquid, which is taken as zero at  $T = 0$ ). The relationship was obtained by H. London by another method, and has been very thoroughly tested experimentally. This may be regarded as a check on the idea, supported by other evidence also, that the superfluid carries no entropy

Now suppose that we establish steady conditions and then gradually widen the slit connecting the two vessels. It now becomes possible for the *normal* fluid to flow through the slit under the influence of the pressure difference. The position now becomes analogous to that of an attempt at the measurement of osmotic pressure with a "leaky" semipermeable membrane that lets some of the solute through. The end result would be an equal concentration on both sides of the membrane and no osmotic pressure. If, however, fresh solute were supplied as fast as it diffuses through the membrane a pressure difference would persist. We can carry out just such an experiment by supplying heat on the high pressure side of the slit. Because of the difference in temperature, the concentration of superfluid is less on this side, so superfluid can travel through the slit to try and redress the balance. However, it absorbs some heat from the supply and some of it is converted into normal fluid. The normal fluid then moves back towards the cold side under the influence of the pressure difference. We can compute the rate of flow using Poiseuille's law (neglecting any mutual force between the two fluids) and the rate of heat transfer then follows if we know the heat capacity. Since the rate of flow is proportional to  $\Delta P$ , and  $\Delta P$  is proportional to  $\Delta T$  by (23), we get a linear law for small rates of heat transfer; this

is not true conduction, but depends on the peculiar convection mechanism of "conveyor belt" type, the superfluid carrying no heat. For small enough  $\Delta T$  we get predictions of the apparent heat conductivity in agreement with experiment, but, if the calculated rate of flow becomes too large this simple treatment ceases to hold, the observed rate of transfer becomes less than that calculated and ceases to be proportional to  $\Delta T$ , and, at the same time (23) ceases to hold. It is natural to suspect some interaction between the two fluids if the velocities rise to too high values; what is surprising is that there seems to be a range of velocities for which there is no measurable interaction of the two fluids, the flow of each seeming to take place just as if the other were not there!

This success in interpreting further experimental facts leads us to ask whether we cannot set up a two-fluid hydrodynamics, assigning a density and a velocity field to each of the fluids, as is already done in the theory of pseudo heat-conduction. This can be done fairly easily as follows: From continuity we have

$$\operatorname{div} (\rho_s \mathbf{v}_s + \rho_n \mathbf{v}_n) + \frac{\partial \rho}{\partial t} = 0. \quad (24)$$

From Newton's second law we conclude that

$$\frac{\partial}{\partial t} \left( \frac{\rho_s \mathbf{v}_s + \rho_n \mathbf{v}_n}{\rho} \right) + \frac{\operatorname{grad} P}{\rho} = 0, \quad (25)$$

these two equations being fairly obvious generalizations of the laws of ordinary hydrodynamics. If we suppose that all the entropy is transported by the normal fluid, we find

$$\frac{\partial}{\partial t} (\rho_n s) + \operatorname{div} (\rho_s \mathbf{v}_n) = 0 \quad (26)$$

while, if we suppose that the superfluid is completely free to move under the influence of the osmotic forces, its acceleration will be proportional to the gradient of the Gibbs function per unit mass, that is

$$\frac{\partial \mathbf{v}_s}{\partial t} + \operatorname{grad} g = 0. \quad (27)$$

This equation has been derived by a physical argument, but can be derived more rigorously by the use of an energy equation, i.e., we suppose that each of the fluids makes its own contribution to the total kinetic energy of the motion. It can be seen that (27) is dimensionally correct, but the first argument we have used cannot exclude the presence of some ratio of densities like  $\rho_s/\rho$ .

Equations (24) and (25) describe mass transfer of *both fluids together* under the influence of pressure gradients, that is to say to ordinary sound waves. If we wanted to discuss situations in which viscosity was not negligible, such as flow through a narrow slit, we should have to add the usual Navier-Stokes terms to (25). Equations (26) and (27) indicate the possibility of another form of flow, *relative motion of the two fluids*, and, since  $\rho_s/\rho_n$  is a function of temperature, we expect this to be associated with *local variations of temperature*. If the velocities and changes of density are small, we may write the left-hand side of (25) as

$$\frac{\rho_s}{\rho} \frac{\partial \mathbf{v}_s}{\partial t} + \frac{\rho_n}{\rho} \frac{\partial \mathbf{v}_n}{\partial t} + \frac{\text{grad } P}{\rho}$$

and we subtract (27) from this, using the equation  $dg = -s dT + dP/\rho$  from thermodynamics, so that

$$s \text{ grad } T = \frac{\rho_n}{\rho} \frac{\partial}{\partial t} (\mathbf{v}_s - \mathbf{v}_n) \quad (28)$$

Substituting  $\partial \rho/\partial t$  from (25) into (26) and again dropping second-order terms, we find

$$\rho \frac{\partial s}{\partial t} + s \rho_s \text{ div } (\mathbf{v}_s - \mathbf{v}_n) = 0. \quad (29)$$

To complete the theory of this type of motion, we need a relation between  $s$  and  $T$ , just as we need a relation between  $P$  and  $\rho$  to complete the theory of ordinary sound. Now, the coefficient of expansion of liquid He II can usually be neglected, in other words the entropy depends almost entirely on the temperature and very little on the pressure. [ $(\partial s/\partial P)_T$  is equal to  $-(\partial v/\partial T)_P$  by one of Maxwell's thermodynamic relations] Furthermore, with a small coefficient of expansion the specific heat at constant volume and constant pressure are practically the same. Thus we may write  $ds = C_p dT/T$ , and using this to eliminate  $T$  from (28) we can eliminate  $s$  (or  $\mathbf{v}_s - \mathbf{v}_n$ ) between (28) and (29), and we arrive finally at a *wave equation*, with velocity of propagation given by

$$C_2^2 = \frac{\rho_s}{\rho_n} \frac{T s^2}{C_p}. \quad (30)$$

This velocity is usually known as the *velocity of second sound*, on account of the formal analogy between Eqs. (28) and (29) and the theory of ordinary sound. Actually the prediction is that temperature differences can be propagated in a *wavelike* fashion by virtue of the relative motion of the two

fluids. This phenomenon was predicted theoretically by Tisza and Landau and has been verified experimentally. It is something essentially different from a high heat conductivity. A little experience with the ordinary heat conduction equation soon convinces one that, no matter how high a numerical value we give to the conductivity, a large attenuation of any "temperature wave" must occur in a distance of the order of a wavelength, whereas the experimental result with "second sound" is that waves and pulses can be propagated for many wavelengths without significant attenuation. In certain conditions the modes of motion corresponding to ordinary and second sound became *coupled*, and are no longer independent of one another, but there is a wide range of conditions for which they are practically independent. Thus, once again the two-fluid concept is successful in interpreting observed facts so that it becomes almost certain that it has some physical basis, in spite of its artificiality.

### 3.4 What is the Superfluid?

A hint on the possible nature of the superfluid is given by the theory of Bose-Einstein condensation outlined above. This phenomenon occurs for a large class of assemblies, and it is very tempting to regard the state of lowest energy as being related to the superfluid. The observed absence of entropy transfer associated with flow of the superfluid is then nicely accounted for, as is the variation of  $\rho_s/\rho_n$  with temperature, the transition temperature, at which  $\rho_s$  becomes zero, being identified with the temperature at which condensation sets in and atoms start "crowding into" the very lowest level. There is little doubt that this view is, in substance, correct, but it leaves certain things unexplained. For example, it is not at all obvious why a molecularly rough solid should be able to slide past such an assembly without dragging along some of the atoms that are occupying the very lowest level. Some light is thrown on this question by an alternative derivation of  $\rho_n$ , due to Landau. His argument applies to any model, but, for simplicity, we consider the Debye-like model. The fundamental point is that the excitations can, in such a model, be considered to resemble sound waves, though we do not, as yet, know very much about the actual form of the wave functions and, as we have seen, we obtain very similar energy spectra from a variety of models. To account for the observed pressure of sound, one must suppose that a sound quantum "carries" momentum as well as energy, though it is not always obvious that this is so. For example, in the "solid-like" model, *all* momentum of an assembly is apparently associated with the one variable  $C_0$ , and none with the variables  $C_s$  and  $S_s$ . (See p. 429).



The state of affairs considered by Landau was that of a solid boundary moving tangentially relative to the assembly. This is a fair idealization of, say, liquid flowing through a tube, or a disk oscillating in the liquid. We ask what is the situation when the motion has gone on long enough for conditions to have become steady. In an ordinary liquid, the layers immediately in contact with the solid would be moving with it, while those further away would be moving less rapidly. In a gas, some "slip" can occur even at the boundary. For simplicity, we restrict ourselves to the case of a single velocity of sound and low temperatures. A sound quantum of energy  $h\nu$  will be assigned a momentum  $h\nu/c$  which may be in any direction, and we wish to find the mean momentum of a layer of liquid in contact with a solid boundary moving with a tangential velocity  $v$ . We can derive the result by either of two practically equivalent arguments.

We may say that the apparent frequency of a quantum moving in a direction inclined at an angle  $\theta$  to the wall will be modified by the Doppler factor  $1 - v \cos \theta/c$  when observed from a point fixed in the wall, from which it follows that there must be corresponding changes in the energy and Boltzmann factors for such a quantum. Or we may be more sophisticated, and say that we specify in advance the total momentum of the liquid in the  $x$  direction, compute the mean energy of the assembly as a function of this momentum, and then compute the corresponding velocity of translation by means of the relationship  $v_x = \partial E / \partial P_x$ . This is a somewhat more complicated argument, using the general theory of selector variables in statistical mechanics, but leads to exactly the same result in practice. For the total momentum, we find the result

$$= \int \frac{4\pi}{c^3} \nu^2 d\nu \int_0^{\pi/2} \frac{h\nu \cos \theta}{c} \exp \left[ \frac{\sin \theta d\theta}{\frac{h\nu(1 - v \cos \theta/c)}{kT} - 1} \right] \quad (31)$$

where the first factor represents the number of possible frequencies in the range  $\nu$  to  $\nu + d\nu$  for an assembly of unit volume that occurs in the ordinary Debye theory, while the final factor represents the modified Planck function. Expanding in powers of  $v/c$  and retaining only the first order term, we find for  $T$  small

$$\frac{\bar{P}_x}{v} = \frac{32\pi k^4 T^4}{\hbar^3 C^5} \quad (32)$$

It will be noticed that this vanishes with  $T$ . This expression is of the dimensions of a momentum per unit volume divided by a velocity and we are thus tempted to identify it with  $\rho_n$ , the density of normal fluid. Numerical

comparison with values of  $\rho_n$  deduced from measurements of  $C_2$ , the velocity of second sound, by the use of formula (30), shows that the simple Debye-like model is a good approximation below about 0.6 °K but that, at higher temperatures, other excitations besides ordinary sound quanta have to be considered also. This is reasonable — we have already noticed the difficulty of finding what, in a liquid, correspond to transverse elastic waves in a solid. If we accept this model quite literally, using (32) for  $\rho_n$ , and calculating the entropy according to the ordinary Debye theory, we find the result  $C_2 \rightarrow C_1/\sqrt{3}$  as  $T \rightarrow 0$ . This prediction was, at one time, thought to have been accurately confirmed experimentally,  $C_2$  and  $C_1$  having, apparently, both “levelled off” by about 0.5 °K, but more recent work suggests that  $C_2$  rises to a limiting value in the neighbourhood of  $C_1$ . This does *not* contradict the simple model, since there are many reasons for thinking that the approximation of regarding the two modes of motion as independent fails at the very lowest temperatures; for example, the effects of *true* heat conductivity, viscosity and long mean free paths of the sound quanta all seem to intervene in much the same range of temperatures (below about 0.4 °K). Any one of these can, in principle lead to *coupling* between the two modes of motion.

It is possible to carry the idea of treating the total momentum  $P_z$  and the velocity  $v$  as a pair of thermodynamically conjugate variables a little further. For example, one can calculate the mean energy as a function of  $v$  and one obtains an additional term  $\frac{1}{2}\rho_n v^2$  per unit volume, as one might expect. One can further show that the entire entropy of the sound field is transported with the velocity  $v$ , thus obtaining a theoretical justification for Eqs. (26) and (27) which were originally obtained as deductions from experiment. Thus, we arrive at the idea that the quantity  $\rho_n$  is a measure of the departure of the helium from its ground level. In a Debye-like model, we must be careful to avoid the phrase “number of excited atoms,” which is sensible for a gaslike type of model, because the excitation of a single quantum of sound involves a great many atoms. The problem of “describing” the superfluid then becomes practically equivalent to that of finding a good approximation for the ground state wave function in the many-body problem. For the solidlike model, this is easy; the work on p. 429 showed that the coordinates  $C_s$ ,  $S_s$  obey a simple harmonic oscillator type of wave equation, and the wave function of lowest energy is then a product of Gaussian functions, one for each coordinate. In the plasma-like model (p. 442) the coordinates  $q_k$  obey, approximately, the same type of equation, so the lowest wave function for this model is also a product of Gaussian functions, but this time of the  $q_k$ ’s. However, both these models, are, as we have seen, probably rather rough approximations, and it is possible, as

Bijl and Feynman showed, to deduce qualitatively the form of the energy spectrum without any knowledge at all of the ground state wave function. It need hardly be said that the gaslike model also gives little information on this point, since it neglects correlations in the positions of atoms altogether. Attempts have been made to improve this, but they are still rather tentative.

Of much more interest than the quantum mechanical description of the superfluid is the search for an explanation of why superfluid effects occur, or, to put it in another way, why it is possible for the superfluid to flow at finite velocity without the occurrence of irreversible effects? The issue is somewhat confused because the theory of transport effects in ordinary assemblies is not yet in a completely satisfactory state. If, for example, we study the "Hookes' Law solid," we can solve its wave equation rigorously, and determine its "stationary states." This, however, implies that a sound-quantum once excited would persist for ever, and have a very long mean free path, and this seems to remain true even if we introduce cubic or quartic functions of the displacements of the atoms into the expression for the energy. Thus, it is usually necessary to assume arbitrarily the existence of a finite "phonon mean free path," which is difficult to calculate so we seem to be faced with the double task of explaining the existence of this in ordinary assemblies, and then having done this, to account for the existence of reversible effects in liquid helium II.

Subject to this, the accepted explanation of superfluid behaviour runs as follows. A *finite* tangential boundary velocity is required to create new excitations.

(1) Because of the symmetry between atoms, Feynman<sup>9</sup> showed that the only excitations of low energy are phonons, corresponding to small local compressions of matter and the consequent movement of many atoms. The macroscopic motion of a single atom, and the consequential motion of a few others near it corresponds to large values of  $h$  in the Bijl-Feynman treatment (p. 440) and therefore to higher energies ("rotons"). The exchange of positions of several atoms "following one another round a ring" does not lead to anything new, because, according to the identity principle, the final state is the same as the initial one.

(2) Rough calculations by Landau<sup>1</sup> showed that it would be a difficult matter to excite another phonon in a Debye-like liquid by the tangential motion of a rough solid past it, a velocity of the order of the velocity of sound apparently being required to excite a phonon. A roton would still require velocities of the order of metres per second, compared with observed critical velocities of the order of *centimetres* per second at which irreversible effects set in for experiments in flow through slits.

(3) As a result of recent experiments, it is now believed that the tangential motion of a solid boundary leads to the appearance in the superfluid, of *quantized vortex filaments*. This was originally predicted by Onsager from a purely hydrodynamic picture. Their proper quantum mechanical description in a real, discontinuous fluid is not yet possible, but their physical existence in liquid helium that is being strongly sheared, or rotated above critical velocity, seems to be established beyond all doubt by experiments in which pseudo heat-conduction and the propagation of second sound are shown to be affected by such motion — a discovery of Kapitza's. The observed effects can be explained reasonably well on the basis that the phonons and rotons are *scattered by the vortex filaments* (in addition to the scattering of phonons and rotons by one another, which is the accepted explanation of the ordinary phenomena of viscosity and the absorption of first and second sound, the details of which have been worked out very elaborately by Landau and Khalatnikov. The agreement with experiment is good, although a number of parameters have to be chosen arbitrarily).

The vortex filaments seem to differ in an important respect from the phonons and rotons, in that they are not *permanently* present in the liquid. (According to the Debye model of a liquid or solid at a finite temperature, sound quanta are always present, the numbers of quanta of each frequency fluctuating about mean values in the usual way.) However, if liquid helium is rotated or sheared, and then left, experiments on the propagation of second sound shown that it gradually reverts to its "virgin" state in a time of the order of minutes. This is attributed to the very slow decay of vortex filaments once they have been formed. The mechanism may be essentially the same as the decay of turbulence in an ordinary liquid, but very little is actually known about it. It seems to require a finite, but very small, viscosity of the superfluid. Feynman has suggested that the vortex lines eventually break up into rotons, but this is only a speculation at present.

The "imperfect Bose-gas" model of the liquid is by no means dead. Much of the work summarized above could have been based on this model as a starting point. In its present form, it does not lead itself very well to predicting numerical values for irreversible effects such as viscosity and absorption of sound, simply because we do not know how to set up such calculations in a gas-like assembly with strong interactions. There is some evidence that, at all events, near the transition temperature the gaslike model is preferable to the Debye-like model. The latter does not predict a discontinuous transition when  $\rho_n$  becomes equal to  $\rho$  at all, but such a result follows naturally from the gaslike model. Indeed, Landau<sup>1</sup> had to assume, quite arbitrarily, that his Debye-like model *broke down* at the transition

temperature. However, such a model is wanted for liquids in general, and for He I in particular, which it seems capable of describing quite well, and it is a pity to have to abandon it simply because it is already in use for He II.\*

It also seems likely that the gaslike model can be helpful in understanding the flow under small pressure differences; the ground level of a perfect gas being strongly affected by a gravitational field; the appropriate wave function is confined to a distance from the bottom of the vessel of the order of  $10^{-4}$  cm, instead of spreading throughout the vessel as it does in the absence of a field. It seems unlikely that the interatomic interactions obliterate *all* traces of this very violent effect. The model is also likely to be of help in discussing the interaction with solid boundaries. The interesting point here is that the interaction between two helium atoms is about enough to lead to a bound level, so that the liquid may contain aggregates of small numbers of atoms resembling the deuteron in having no excited state. The collision of such an aggregate with a solid boundary differs essentially from that of an ordinary molecule (which can suffer changes in its vibrational — rotational degrees of freedom, and can therefore carry up entropy to a solid boundary, or carry it away) but an aggregate devoid of excited levels can have no such internal store of entropy.

### 3.5 Film Phenomena

Much work has been done on the thick absorbed film, of the order of 100 atoms thick, discovered by Rollin. It seems to cover *any* solid surface to which liquid He II has access, and it shows superfluid properties very like those of the bulk liquid. This fact leads to some rather spectacular effects like “flowing uphill.” A surface dipped in He II is rapidly covered, and, if a path to another vessel at a lower level is available, the liquid transfers itself to it, the flow being capable of taking place even if the difference in levels is a fraction of a millimeter and the barrier is several centimetres high. Various theories of the film have been proposed, mostly involving modifications of existing models of adsorption intended for thin films and high adsorption energies, but the present tendency is to regard the film as closely akin to bulk liquid, its properties being modified by the effect of the van der Waals attraction of the walls. These effects are by no means negligible, even though these forces are very weak in comparison with other substances. It is probable, for example, that their effect is equivalent to a pressure sufficient to solidify the four or five layers nearest the wall. At

\* See Temperley<sup>10</sup> for an account of the strengths and weaknesses of the two models.

one time, it was thought that there was a sharp drop in thickness at the transition temperature, and this led to various suggestions that the sudden thickening of the film was a manifestation of Bose-Einstein condensation of the liquid, the atoms in the very lowest liquid level forming a convenient and inexhaustible supply of atoms for adsorption. However, it has recently been shown that films of about the same thickness can be formed with He I, provided that great precautions are taken to keep out radiation. The general tendency now is to regard the superfluidity, rather than the Bose condensation, as the explanation. A thick film does not normally occur for He I because the atoms are readily knocked off by radiation, and cannot be quickly replaced, but in He II the superfluid flow does permit true equilibrium to be attained very quickly, which is notoriously difficult to attain in an ordinary adsorption experiment. The variation of thickness with height above the bulk liquid is then the result of the competing claims of gravity and the van der Waals attraction. Put in another way, the vapour at some distance above the liquid is slightly unsaturated, because of the pressure head  $\rho gh$  associated with a column of vapour of height  $h$ , so the layer of absorbed liquid in equilibrium with it is slightly thinner than for a portion of the same solid very near the liquid free surface.

### 3.6 Liquid He<sub>3</sub>

The properties of this liquid were eagerly studied as soon as it became available, in order to test the hypothesis that He<sub>4</sub>, being a "quantum liquid," should owe some at least of its properties to the symmetry properties of its wave functions. It was soon found that superfluid properties were absent, the viscosity seeming to behave like that of an ordinary liquid, so that the above view seemed to be confirmed, but the liquid quickly became an interesting theoretical problem in its own right. The most natural idea is to try to modify the theory of a Fermi gas, which even in its crudest form has given good results in the theory of metals. Another point of interest is the connection with the problem of nuclear matter (Vol. III, Chapter 5). In both cases we have an interaction that is probably attractive with a repulsive "core" and is of about the right strength to lead to a bound state for two interacting particles, an excited state being absent. Now, in spite of the fact that an interaction as strong as this cannot be neglected, it has been found that quite crude models of the nucleus can give worthwhile results. For example, we can consider the motion of all the nucleons in a "smoothed-out" field, leading to the "shell model." Thus, we might hope that this liquid could be regarded as a simplified "scale model." One

consequence of Fermi statistics is that, apart from the effect of interactions, wave functions tend to be small when two particles approach one another. This means that the details of the interaction function probably play a less important part than they do in  $\text{He}_4$ , where the effect of the statistics is to give an apparent *attraction*, and, as we have seen above, it is quite likely that loosely bound aggregates of two or three atoms are physically present in the liquid. (In the nucleus, one sometimes thinks of the presence of "virtual  $\alpha$ -particles," but this is because their binding is very strong, and it is much less useful to think of virtual deuterons or tritons.)

An experimental fact that is not available for  $\text{He}_4$  is that it is possible to measure the magnetic properties indirectly by using the techniques of nuclear resonance. Thus, it is possible to test whether the system of interacting spins behaves in the ways that the theory of a partially degenerate Fermi gas would suggest. We say partially degenerate because, in the absence of interactions, the Fermi temperature of liquid  $\text{He}_3$  of the observed density would be about 5°K, so that it seems that here at last we have a Fermi assembly with a reasonably accessible Fermi temperature. However, the results of various attempts to "hot-up" the conventional theory of a Fermi gas in order to allow for the interactions have been rather disappointing. It is possible to introduce van der Waals like terms to try to allow for the interactions and finite size of the atoms. This model can, in certain circumstances, predict two transitions that one can identify with liquefaction and solidification, and behaves in the way that such models usually do; one fixes the constants from some properties, whereupon others are predicted in order of magnitude. There have also been various attempts to combine the Fermi model with a Debye-like model, making use of the observed compressibility when it became available. (Even a perfect Fermi gas has a finite compressibility as a result of the exclusion principle, so it is difficult to say whether the compressibility is mainly determined by this, or by the interactions. The zero-point energy is also finite even if there are no interactions, so the "blowing-up" effect that occurs with  $\text{He}_4$  is present here also.) We can develop the model in various ways, either postulating the simultaneous presence of the two types of excitation, or we can attempt a detailed model, in which some of the atoms are supposed to form a quasi-crystalline lattice, while others form the Fermi gas. It is, however, not easy to find such a model agreeing *both* with the specific heat and the susceptibility data, the latter suggesting a much lower Fermi temperature than does the former.

Another model that is successful in describing most of what is known about the liquid is the "pair" model. At very low temperatures, the excita-

tions of most importance are those associated with pairs of atoms moving in a smoothed field, and a reasonable guess<sup>10</sup> about the distribution of these levels, based on the Heitler-London picture of the hydrogen molecule, is capable of accounting both for the specific heat and susceptibility. At "high" temperatures, collective excitations take over, and we have, effectively, the Debye model once again. It is interesting that this situation is just the reverse of that in  $\text{He}_4$ . Here the "low" temperature excitations are generally agreed to be sound quanta, and it is also agreed that the high temperature excitations each involve only a few atoms. The "pair" model has been developed further by Brueckner's method. At very low temperatures, he arrives at substantially the Fermi-gas picture, but with the important generalization that the actual mass of the atoms is replaced by an "effective mass" which is not constant but varies with density. With such a model the specific heat and the susceptibility are not "tied together" in the way that they are in the simpler Fermi models, thus removing one of the great difficulties confronting the latter. In fact, it is difficult to calculate the susceptibility properly as, unlike some of the properties of an assembly of antisymmetrical particles, this turns out to be rather sensitive to the details of the interaction.



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